

CONTRIBUTIONS TO (DIENE)Fe(CO)₃ CHEMISTRY

I. Synthesis of Functionalized Complexes and
their Use in Polyene Synthesis

II. Selective Decarbonylation Reactions with
Concomitant Ligand Exchange

Inaugural-Dissertation

submitted for the
degree of Doctor of Philosophy
to the Philosophical Faculty II
of the
University of Zurich

by
Christoph M. Adams
of Basle (BS)

approved by Prof. Dr. W. von Philipsborn

Zurich 1987
Zentralstelle der Studentenschaft

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For Jane, Steven and Kelly

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The successful completion of any task depends to a large extent on the people with whom one works. I consider myself very fortunate to have been part of an enthusiastic, trustful and highly qualified team in which good friendships have developed over the years.

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1. INTRODUCTION

The development of organometallic chemistry in the past three decades has been rapid and very fruitful. The synthesis and structure determination of ferrocene [1] and the discovery of the Ziegler-Natta process [2] in the early fifties triggered the growth of organotransition metal chemistry. The Wacker process [3], in which ethylene is converted into acetaldehyde, had a profound impact on the rapidly developing petrochemical industry at that time. An unprecedented number of complexes with novel structures such as Vaska's complex $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$ **1** [4], Fischer's carbene complexes **2** [5] and dinitrogen fixation complexes **3** [6] were synthesized. The discovery of Wilkinson's catalyst $\text{RhCl}(\text{PPh}_3)_3$ **4** for the hydrogenation of olefins was a milestone in the field of homogeneous catalysis [7] (Fig. 1).

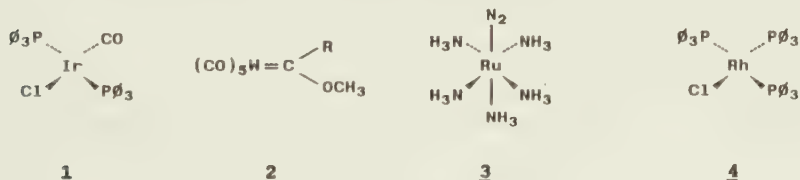


Figure 1

Organotransition metal compounds may be broadly classified as those having either M-C σ -bonds or M-C π -bonds. The nature of the M-C bond is strongly influenced by the ligands attached to the metal. Electron-withdrawing ligands coordinated to the metal cause an increase in the electronegativity of the metal fragment while electron-donating ligands exert the opposite effect. The concept of π -bonding was proposed first by Dewar [8] describing the silver-olefin bond and later extended by Chatt

and Duncanson [9] to other transition metals such as platinum. This model proposes two basic interactions between metal and olefin to describe the bonding :

- a) Overlap of an olefin π orbital with an empty metal d-orbital
- b) Overlap of a filled metal d orbital with the empty olefin π^* orbital
(electron back donation from the metal to the olefin)

On coordination to a metal the chemical properties of the olefin are influenced depending on the extent of olefin-to-metal electron donation and metal-to-olefin back donation. When the olefin is coordinated to a charged metal ion or when the metal is in a high positive oxidation state there is an electron drift from olefin to metal thus making the coordinated olefin more susceptible to nucleophilic attack. When the olefin is coordinated to a low-valent transition metal, the contribution of back bonding is more pronounced and the carbon-carbon double bond of the olefin is lengthened. In the case of (butadiene) $\text{Fe}(\text{CO})_3$ three possible valence-bond representations A, B and C can be envisaged (Fig. 2).

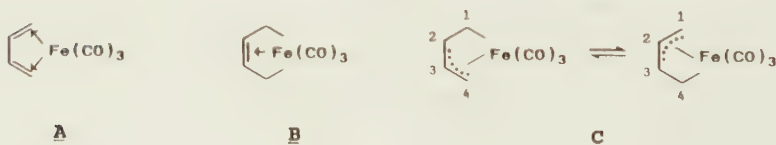


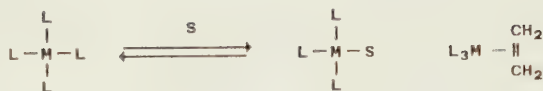
Figure 2

The butadiene ligand has s-cis form and the four C-atoms are approximately equidistant from the iron. This suggests that resonance structure **A** is more plausible. On the other hand, with an increase of metal-to-butadiene back donation, the carbon-carbon bond order alternation approaches the long-short-long pattern. This corresponds to resonance structure **B** with two σ -Fe-CH₂ bonds and one π -Fe-olefin bond. Evidence from X-ray structure analysis confirms this as all terminal substituents of the diene are distorted out of plane. This can be considered as a partial rehybridization of the carbon atom from sp² to sp³. For the asymmetric structures **C** a fast interconversion of two enantiomeric forms is proposed, in which the butadiene ligand is bound by one σ -bond and one allylic π -bond to the metal [10,11].

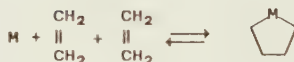
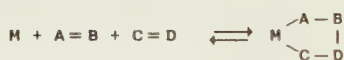
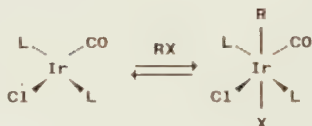
In contrast to conventional organic syntheses, the fundamental processes in reactions of organotransition metal complexes include ligand coordination and dissociation (I), oxidative addition and reductive elimination (II), insertion and extrusion (III) as well as reactions of coordinated ligands (IV). These processes are shown in Figure 3.

The complexation of an unsaturated molecule to a transition metal can significantly change the reactivity of the molecule and influence the regioselectivity and stereoselectivity of a reaction course. Molecules of theoretical interest and intermediates of practical value which are too unstable to be isolated can be stabilized and double bonds can be protected from unwanted reactions. The extent of the influence depends on the complexing transition metal as well as on the other ligands bound. Organoiron complexes have shown considerable potential in all these respects and their synthetic application has become

(I)



(II)



(III)



(IV)

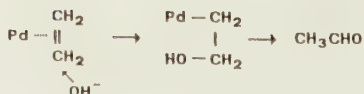


Figure 3

quite widespread for a number of reasons :

- a) they are readily available from a variety of cheap starting materials, such as FeCl_2 , FeCl_3 , ferrocene and $\text{Fe}(\text{CO})_5$,
- b) they are easily handled - conventional Schlenk technique is sufficient for most compounds, and
- c) the iron protecting group is often readily removed by a variety of oxidative methods.

The interest of synthetic chemists in the past few years has also been directed towards the application of organoiron complexes in asymmetric synthesis. In particular, compounds of type $\text{CpFe}(\text{CO})(\text{PPh}_3)(\text{R})$ [12,13,14] have been shown to be of great synthetic value. The synthetic applications of substituted $[\eta^5\text{-(cyclohexadienyl)Fe}(\text{CO})_3]^+$ complexes has been amply demonstrated by the work of Birch [15] and Pearson [16]. The coordination of an iron tricarbonyl fragment to an unsymmetrical diolefin not only reduces the reactivity of the π -system but also converts it to a chiral synthon. It is therefore possible to generate new chiral centers in diastereoselective reactions [17,18].

This thesis is divided into three major parts :

1. Investigation of the reactions of a number of bifunctionalized $(\text{isoprene})\text{Fe}(\text{CO})_3$ complexes and their synthetic utility in the synthesis of polyene compounds.
2. Furthermore, variation of the $\text{Fe}(\text{CO})_3$ protecting group by selective decarbonylations with concomitant ligand replacement was investigated.
3. In a spectroscopic study ^{57}Fe NMR was applied to determine substituent effects in a series of $(\text{enone})\text{Fe}(\text{CO})_3$ complexes on the ^{57}Fe chemical shift.

2. ORGANOIRON COMPOUNDS IN ORGANIC SYNTHESIS - AN OVERVIEW

2.1 Iron Carbonyls

Over the years, iron carbonyls have played a central role in the development of carbonyl chemistry and today they represent one of the largest classes of transition metal carbonyl complexes. The simplest stable iron carbonyl compound $\text{Fe}(\text{CO})_5$ 5 was discovered independently by Mond [19] and Berthelot [20] in 1891. This highly toxic compound with a high vapour pressure is prepared by the direct reaction of carbon monoxide with finely powdered iron at elevated temperature and pressure. From low temperature electron diffraction measurements a trigonal bipyramidal structure has been proposed with axial and equatorial bonds of equal length (Fig. 4). The photolysis of $\text{Fe}(\text{CO})_5$ 5 in a low temperature inert gas matrix produces $\text{Fe}(\text{CO})_4$ [21] which is the coordinatively unsaturated intermediate in complexation reactions.

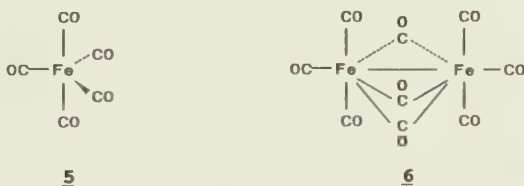


Figure 4

The first binuclear carbonyl compound to be isolated and x-rayed was $\text{Fe}_2(\text{CO})_9$ 6 [22,23]. This very useful source of the $\text{Fe}(\text{CO})_4$ moiety is synthesized most conveniently by the photolysis of $\text{Fe}(\text{CO})_5$ in cooled glacial acetic acid with a medium pressure mercury lamp [24]. The structure of diironnonacarbonyl shown in

Figure 4 contains three carbon monoxide ligands bridging two metal atoms joined by a metal-metal bond. The remaining carbon monoxide ligands are bound evenly to the two metals. The thermal dissociation of $\text{Fe}_2(\text{CO})_9$ in ether or benzene yields $\text{Fe}(\text{CO})_5$ and $\text{Fe}(\text{CO})_4$, the latter being the reactive species.

2.2 Synthesis of $(\eta^4\text{-Diene})\text{Fe}(\text{CO})_3$ Complexes

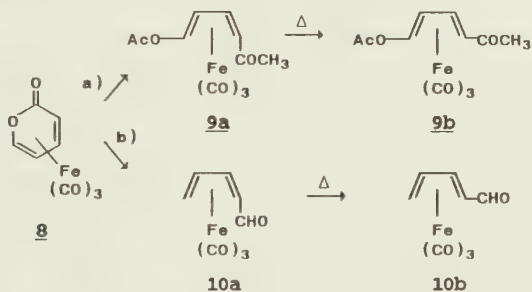
Coordination of 1,3-dienes to a $\text{Fe}(\text{CO})_3$ group provides a means of moderating the reactivity of the unsaturated system to catalytic hydrogenation, hydroboration, electrophilic and Diels-Alder reactions. It also introduces a bulky group which permits the control of the stereochemical course of the reaction and the stabilization of otherwise highly reactive or unstable molecules. A variety of complexation methods are available. Photolysis of $\text{Fe}(\text{CO})_5$ in benzene [25,26,27] in the presence of conjugated and unconjugated dienes needs long reaction times and can result in (Z)-(E) isomerizations, in double bond migration, in formation of $(\text{diene})_2\text{Fe}(\text{CO})$ complexes [28] and also in decomposition of already formed complexes.

Thermal reactions of $\text{Fe}_2(\text{CO})_9$ [29] or $\text{Fe}_3(\text{CO})_{12}$ [30] with dienes as well as the reaction of $\text{Fe}(\text{CO})_5$ with a controlled amount of trimethylamine oxide [31,32] in the presence of a conjugated diene have been successfully applied. The latter reaction occurs smoothly at room temperature or lower but requires the diene to be inert to the amine oxide. In the absence of alkenes, $\text{Fe}(\text{CO})_4(\text{NMe}_3)$ **7** is formed and presumably this could be used for complexation. A nucleophilic attack of Me_3NO at a carbonyl carbon followed by elimination of carbon dioxide takes place.



More recently, the transfer of the $\text{Fe}(\text{CO})_3$ moiety from (hetero-diene) $\text{Fe}(\text{CO})_3$ complexes to conjugated dienes has proven suitable when dienes were photochemically or thermally unstable [33]. (Enone) $\text{Fe}(\text{CO})_3$ complexes have also been used to trap unstable reaction intermediates [34,35].

Substituted butadiene complexes may be prepared from the α -pyrone complex **8** which may be made directly. Nucleophilic addition leads to ring opening and the formation of the less stable (Z)-isomers **9a** and **10a** which are converted thermally to the (E)-isomers **9b** and **10b** (Fig. 5) [36].



a) 1, LiCH_3 11, Ac_2O b) 1, LiAlH_4 11, H_2O

Figure 5

Semmelhack and Park [37] have recently reported that coupling of ethoxy substituted (carbene) $\text{Fe}(\text{CO})_4$ complexes **11** [38] with 1,3-dienes, results in the formation of (η^4 -diene) $\text{Fe}(\text{CO})_3$ complexes of type **13** via an intermediate ferracyclobutane **12** (Fig. 6). These 5-ethoxy substituted compounds are easily protonated to give the highly reactive η^5 -pentadienyl system.

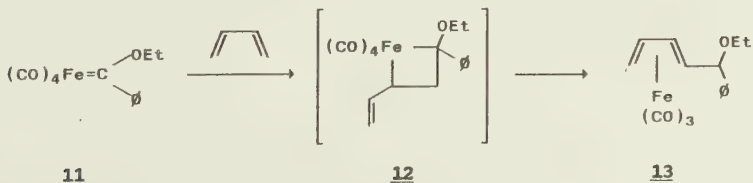


Figure 6

2.3 Synthesis of (η^4 -Heterodiene)Fe(CO)₃ Complexes

α,β -Unsaturated ketones and aldehydes and their corresponding imines form tetracarbonyl and tricarbonyl complexes [39,40,41, 42].

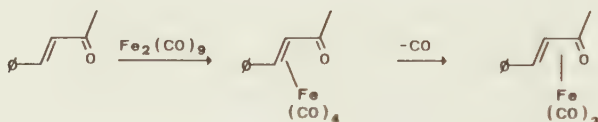


Figure 7

Mild reaction conditions are necessary for the isolation of the tetracarbonyl complexes as they readily lose carbon monoxide (Fig. 7). ((E)-4-phenyl-2-buten-2-one)Fe(CO)₃ **14** has been synthesized in good to excellent yields by refluxing the ligand with $\text{Fe}_2(\text{CO})_9$ [43] in benzene and on irradiation with $\text{Fe}(\text{CO})_5$ [44,45]. The triphenylphosphine substituted analogue of **14** has been prepared by UV photolysis of a solution of $\text{Fe}(\text{CO})_4\text{PPh}_3$ and (E)-4-phenyl-2-buten-2-one and the corresponding triphenylphosphite complex by a thermal reaction of triethyl phosphite with ((E)-4-phenyl-2-buten-2-one)Fe(CO)₃ in benzene [46]. Various more complex α,β -unsaturated ketones have been coordinated in this way.

Isomers of ((+)-pulegone)Fe(CO)₃ **15** with the $\text{Fe}(\text{CO})_3$ group coordinated to opposite faces of the ligand have been obtained but in ((+)-pinocarvone)Fe(CO)₃ **16** and ((-)-3 β -(acetoxypregna-5,16-dien-20-one)Fe(CO)₃ **17** the iron is bound to the same face (Fig. 8a) [47].

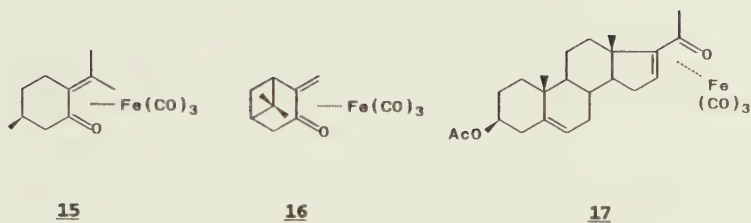


Figure 8a

Prochiral dienes have been reacted with ((+)-pulegone) $\text{Fe}(\text{CO})_3$ 15 and 17 to give complexes of type $(\eta^4\text{-diene})\text{Fe}(\text{CO})_3$ 19 with up to 40% enantiomeric excess. For asymmetric induction to take place an intermediate 18 has been proposed in which the enone and diene are simultaneously coordinated to the same iron atom (Fig. 8b) [48,49]. The steric properties of the enone used determine the degree of induction achieved. A strong interaction between enone complex and complexing diene is necessary for high asymmetric induction. However, a bulky chiral enone can destabilize the intermediate in which case an efficient transfer of the iron moiety does not occur.

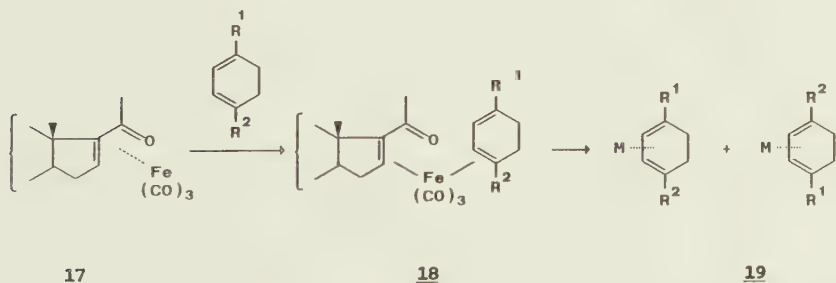


Figure 8b

2.4 Application of Iron Carbonyls in Organic Synthesis

Isomerization of olefins and polyenes can be effected by thermal complexation of a diene substrate to $\text{Fe}(\text{CO})_3$ and subsequent oxidation to yield the rearranged product. This reaction can occur with or without double bond migration. The synthetic utility of this reaction is best illustrated by Corey's synthesis of PG-C₂ **20** (Fig. 9) [50].

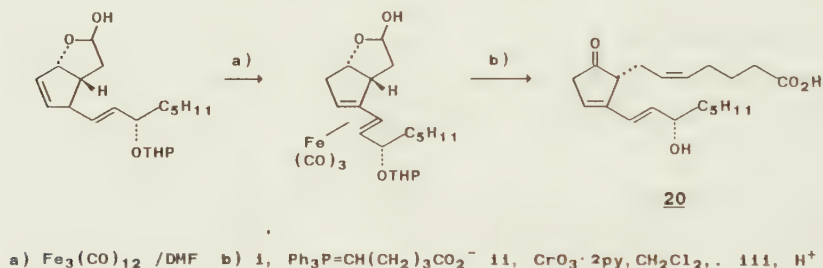


Figure 9

Epoxide ring opening reactions with $\text{Fe}(\text{CO})_5$ are receiving attention with regard to their synthetic utility. Heck synthesized the ferrelactone complex **22** by treatment of the allylic alcohol **21** with $\text{Fe}(\text{CO})_5$ (Fig. 10) [51]. This type of compound was also found in the reaction of vinyloxiranes with iron carbonyls. Churchill et al. [52] found that in contrast to the thermal reaction the photochemical reaction proceeds completely stereospecifically. Subsequent treatment of the ferrelactone complexes with ceric ammonium nitrate results predominantly in the formation of β -lactones. The combination of this knowledge with the known reactions of ferrelactones with amines has been applied in an elegant synthesis of a β -lactam **23** (Fig. 10) [53,54].

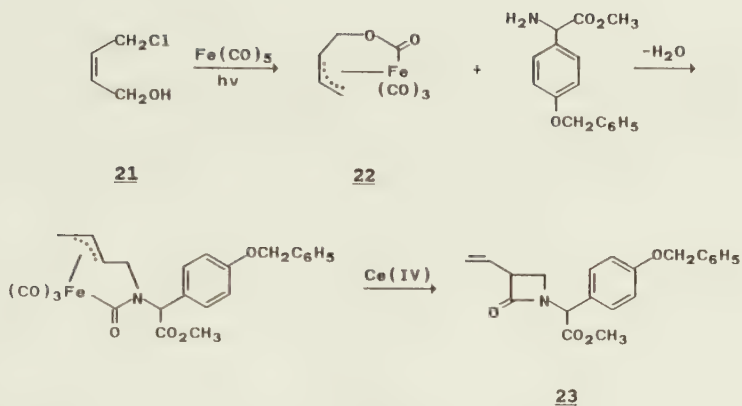


Figure 10

Reactions of $\text{Fe}(\text{CO})_5$ with benzylic geminal halides have been found to result in loss of halogen and coupling to give olefinic compounds in good yields. Noyori and co-workers [55] have extended this reaction to α, α' -dibromoketones 24 and $\alpha, \alpha, \alpha', \alpha'$ -tetrabromoketones 27, which can be dehalogenated by $\text{Fe}(\text{CO})_5$ and $\text{Fe}_2(\text{CO})_9$ to yield a coordinated oxallyl cation 25 which can enter cycloaddition reactions (Fig. 11).

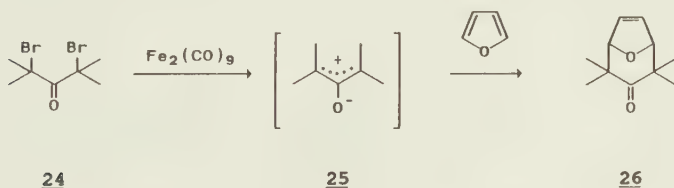


Figure 11

A number of synthetic approaches to natural products and pharmacologically active compounds have been developed, notably the tropane alkaloids 28 (Fig. 12) [56,57].

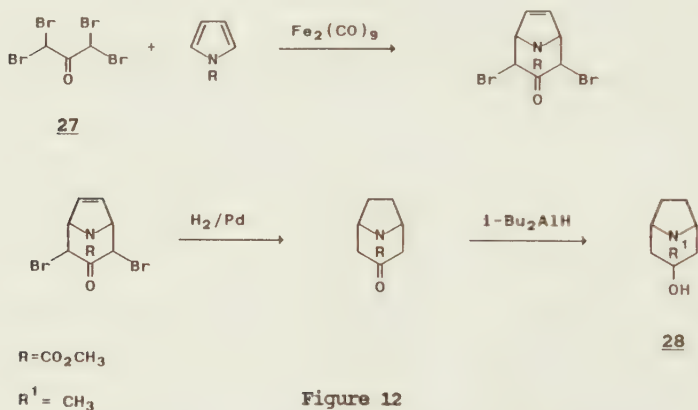
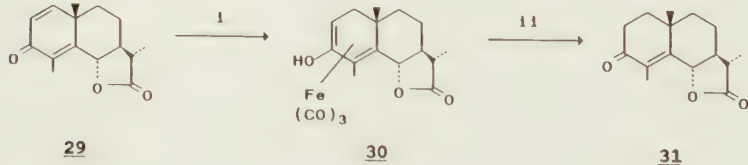


Figure 12

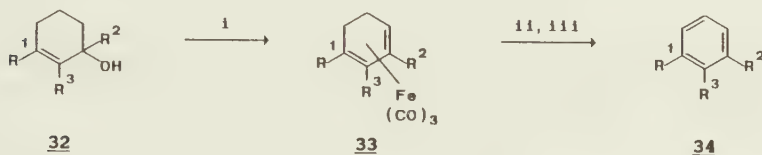
Selective hydrogenation of cross-conjugated cyclohexadienones 29 can be achieved using the $\text{Fe}_2(\text{CO})_9/\text{H}_2\text{O}$ system. Only partial reduction occurs because of the formation of an intermediate (dienol) $\text{Fe}(\text{CO})_3$ complex 30 from which the enone 31 is released on ceric oxidation (Fig. 13) [58].



I, $[\text{Fe}_2(\text{CO})_9]$, H_2O II, Ce(IV)

Figure 13

Readily available cyclohex-2-enols 32 react with $\text{Fe}(\text{CO})_5$ to form the corresponding (cyclohexadiene) $\text{Fe}(\text{CO})_3$ complexes 33. These intermediates can be dehydrogenated to give specifically substituted arenes 34 in good yields (Fig. 14) [59].



i, $[\text{Fe}(\text{CO})_5]$; **ii**, Ph_3C^+ **iii**, $\text{Ce}(\text{IV})$

Figure 14

The reduction of pentacarbonyl iron with sodium amalgam in boiling dioxane results in the formation of disodium tetracarbonyl ferrate $\text{Na}_2[\text{Fe}(\text{CO})_4]$.



This reagent can be used for a number of useful transformations, notably as an acyl anion equivalent by transforming alkyl halides 35 or p-toluenesulphonates into aldehydes or ketones of type 36 in yields of 50-99% (Fig. 15) [60].

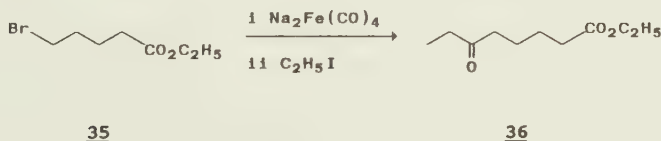


Figure 15

The annelation of halo- or tosyloxy-alkenes with $\text{Na}_2[\text{Fe}(\text{CO})_4]$ results in carbon monoxide insertion and formation of cyclopentanones [61] or cyclohexanones [62]. McMurry's total

synthesis of aphidicolin **39**, a tetracyclic diterpene which shows antiviral activity, included this reaction to convert the tosylate **37** to the cyclohexanone intermediate **38** which had previously been transformed to aphidicolin **39** (Fig. 16) [63,64].

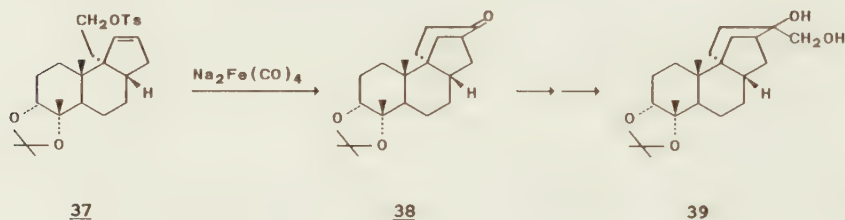
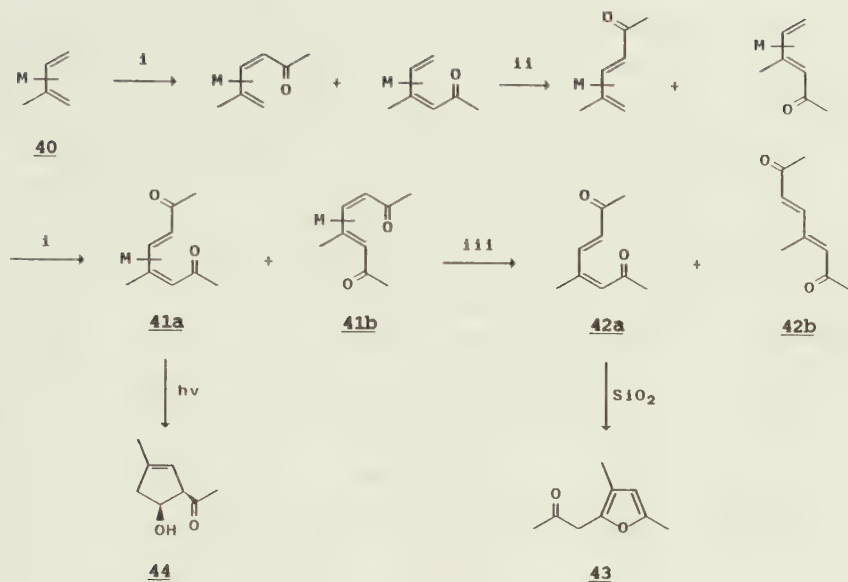


Figure 16

2.5 Electrophilic Substitution Reactions of (Diene) Fe(CO)_3 Complexes

The high reactivity of free polyenes towards acylation reagents is reduced by complexation and permits controlled Friedel-Crafts reactions. (Butadiene) Fe(CO)_3 is acetylated under mild conditions to give mixtures of the (Z)- and (E)-products depending on the work-up adopted [65,66]. Quenching with aqueous ammonia gives only the (Z)-product while use of sodium methoxide causes rearrangement to the more favourable (E)-product. In addition to these Friedel-Crafts type acetylations, Vilsmeier formylations and benzoylations [67] have also been reported. Acetylation of 2-silylated (butadiene) Fe(CO)_3 complexes leads to terminal (Z)-substituted diene complexes. After (Z/E)-isomerization by treatment with acetyl chloride and an aqueous work-up a second (Z)-acetylation occurs at the unsubstituted terminal carbon in moderate to excellent yields [68].



i, $\text{AcCl}/\text{AlCl}_3$ ii, AcCl , RT/ H_2O iii, H_2O_2 , NaOH , MeOH ,

Figure 17

This 1,4-diacetylation of complexed dienes has been extended to (isoprene) $\text{Fe}(\text{CO})_3$ **40** and (2,3-dimethylbutadiene) $\text{Fe}(\text{CO})_3$ complexes. Oxidative decomplexation of the dienediketone complexes **41a** and **41b** with hydrogen peroxide in a methanolic sodium hydroxide solution affords the free dienediones **42a** and **42b**. The (Z)-isomer **42a** cyclizes on treatment with silica gel to give the furan derivative **43**. Reductive photolysis of the dienediketone complex **41a** affords stereospecifically a cis-cyclopentenol **44** in a yield of 79% (Fig. 17) [69].

The stereochemistry of the acetylation of (cyclohexadiene)- $\text{Fe}(\text{CO})_3$ has been the subject of some controversy. Lewis and co-workers [70] reported the formation of the (M)-exo complex while

Gubin and co-worker [71] isolated the (M)-endo product in 45% yield. Pearson has recently shown [72] that the (M)-endo product is found to undergo rearrangement on exposure to alumina. Substitution of a carbon monoxide by a phosphine or phosphite increases the electron density of the metal-diene system thereby facilitating acetylation. Friedel-Crafts acetylation of (cyclohexadiene)Fe(CO)₂(PPh₃) **45** is accomplished in 96% yield to give the (M)-endo product **46** (Fig. 18) [73]. The increased steric hindrance of the triphenylphosphine group does not affect the stereochemical course of the reaction which suggests that the reaction is frontier orbital controlled.

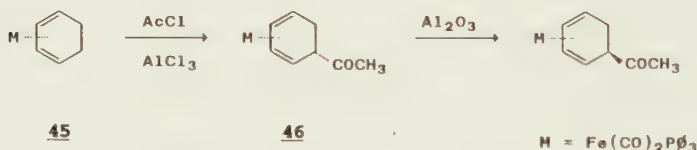


Figure 18

(Diene)Fe(CO)₃ complexes such as (cyclohexadiene)Fe(CO)₃ **47** are susceptible to nucleophilic attack in the presence of carbon monoxide to give metallalactones **48**. Decomplexation of these metallalactones with electrophiles then yields a variety of 3-substituted γ,δ -unsaturated carbonyl compounds **49**. The process is stereoselective with trans-formation of the two new carbon-carbon bonds (Fig. 19) [74,75].

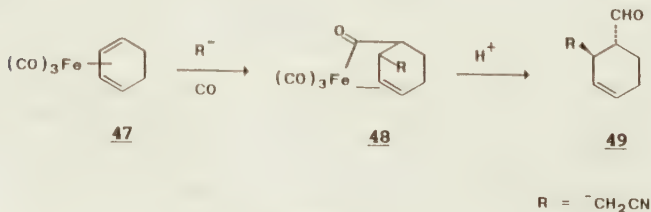


Figure 19

The reductive oligomerization of carbon monoxide to give pentanoic acid has been achieved using $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{P}(\text{CH}_3)_3)_3\text{-(CH}_3\text{)}$ **51** obtained from the hydride reduction of $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2(\text{P}(\text{CH}_3)_3)]^+\text{PF}_6^-$ **50**. This complex undergoes clean homologation on successive treatment with carbon monoxide and borohydride to give $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{P}(\text{CH}_3)_3)(\text{COC}_4\text{H}_9)$ **52** after four carbonylations, which on oxidation yields entirely carbon monoxide derived pentanoic acid (Fig. 20) [76].

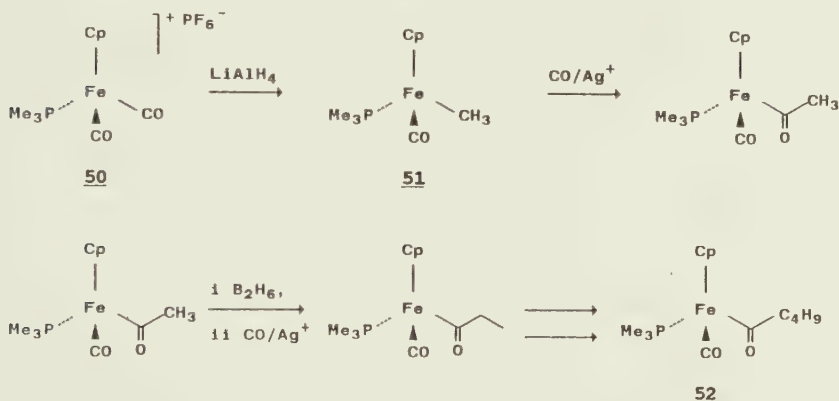


Figure 20

2.6 The Use of $\text{Fe}(\text{CO})_3$ as a Protective and Stabilizing Group

The introduction of a $\text{Fe}(\text{CO})_3$ group into an unsaturated system of three double bonds leaves one double bond of normal reactivity while effectively protecting the other two. The free double bond undergoes carbene additions (Simmons-Smith reaction) [77], facile acetylation [78] and Vilsmeier formylation [79]. Lewis and co-workers have shown that the $\text{Fe}(\text{CO})_3$ group may be used as diene protection during hydroboration, hydration and osmium tetroxide reaction of the uncoordinated double bond in (ergosterylacetate) $\text{Fe}(\text{CO})_3$ **53**. Barton et al. have shown that the

22,23-double bond of the analogous ergosteryl benzoate complex **54** can be hydrogenated using Adams catalyst in the presence of benzyl dimethylsilane (Fig. 21) [80,81].

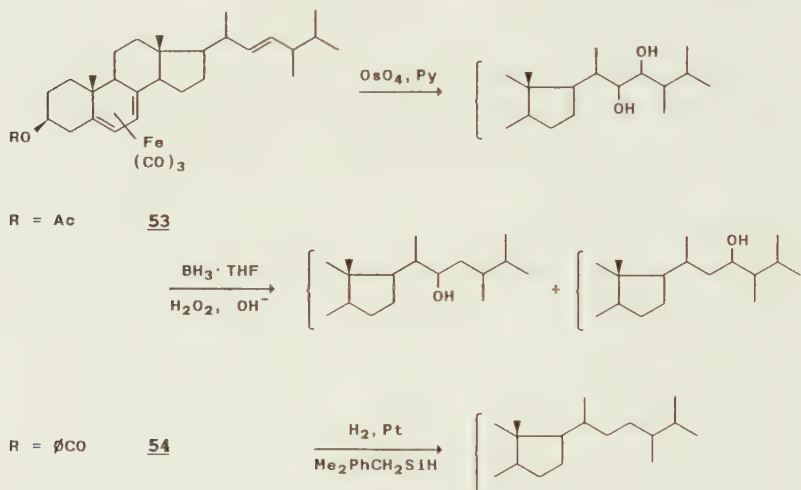


Figure 21

2.7 Decomplexation of (Diene)Fe(CO)₃ Complexes

The efficient disengagement of the transition metal protecting group is a prerequisite for a successful application. Decomplexations of (diene)Fe(CO)₃ complexes have been carried out using oxidation reactions with transition metal salts such as ferric chloride [81], ceric ammonium nitrate [82] cupric chloride [83] in acetone or ethanol or hydrogen peroxide/KOH [84]. Collins reagent [50] and silver(I) salts [85] have also been applied. The above methods have the inherent disadvantage that easily oxidizable functional groups do not survive these conditions. A mild method for the disengagement of organic

ligands has been reported by Shvo and Hazum [86] who treated complexes with large excesses of trialkylamine oxide in aprotic solvents.

2.8 Chiral Iron Complexes in Organic Synthesis

Different types of chirality can be found in chiral iron complexes. The metal can have four different substituents and therefore becomes a chiral centre. The complexation of an unsymmetrical diene to a $\text{Fe}(\text{CO})_3$ group causes planar chirality, while in ferrocenes two different substituents on one of the two Cp-rings is sufficient for metallocene chirality. Furthermore, chiral ligands such as optically active phosphines can be introduced. The synthesis and resolution of chiral iron complexes and their use in enantioselective and diastereoselective synthesis has become quite widespread.

The conversion of alkenes into methyl cyclopropanes can be accomplished via ethylidene transfer from the iron complexes of type $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{CHCH}_3)$ **55a** and **55b** [87]. These complexes must be generated in situ by protonation of the corresponding methyl ether complexes which are obtained from the readily available acyl complexes. The resolved complexes allow the asymmetric methylcyclopropanation of styrene to be carried out with an enantiomeric excess of 85-90% and chemical yield of 75% [14] (Fig. 22).

Brookhart and co-workers have thereby shown that the asymmetric induction emanates primarily from the chirality at the iron centre and that the phosphine chirality plays little or no role at all, which also demonstrates the potential for control by metal configuration in enantioselective catalysis.

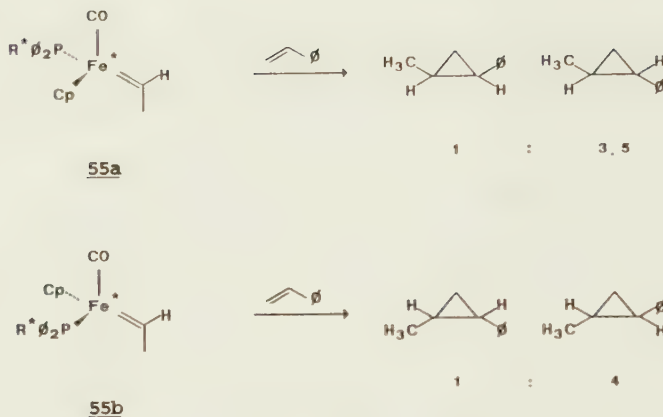


Figure 22

The highly versatile chiral acetyl iron complex **56** has recently been employed by Davies and co-workers [12]. This compound allows excellent stereochemical control to be achieved in a variety of reactions on bonded acyl ligands (Fig. 23). The addition of *n*-butyllithium to the racemic acetyl complex in THF at -78° generates the corresponding (E)-enolate. This enolate can subsequently be utilized in carbon-carbon bond formation reactions e.g. alkylations [88,89,90], aldol additions [91,92], additions to epoxides [93], and imine synthesis [94,95], Diels-Alder reactions [96] and tandem Michael Additions [97]. The high stereoselectivities observed in these alkylations arise because the preferred anti-conformation of the enolate oxygen to carbon monoxide can only be alkylated from the unhindered face. The bulky triphenylphosphine group prevents attack from the opposite face. The enantiomerically pure parent acetyl complex has also been synthesized and its absolute configuration and optical purity determined [98].

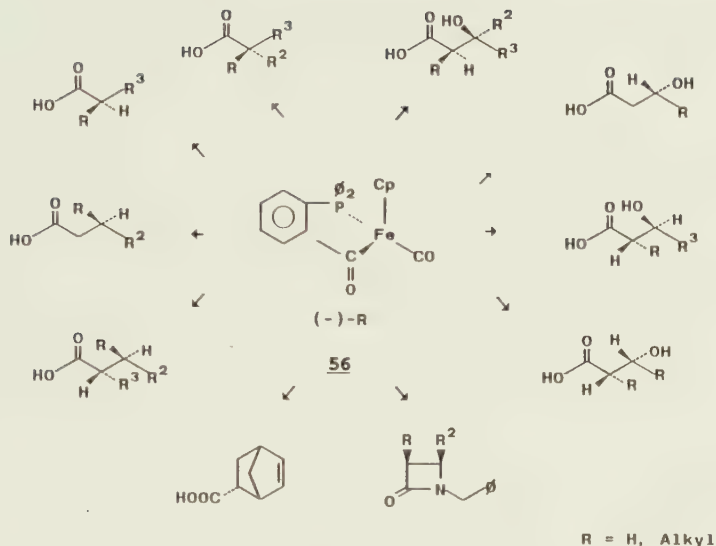


Figure 23

Although optically active ferrocene derivatives have been most extensively investigated [99], only few synthetically useful applications have been reported. Ugi and co-workers [100] have shown that chiral sulfoxides, which can transfer their chirality from sulphur to carbon, can be derived from ferrocene compounds.

Only a few optically active acyclic or cyclic diene complexes have been synthesized. Resolution has been achieved using classical re-crystallization methods of salts of optically active amines such as (-)-brucine [101], (-)-phenylethylamine [102], phenylethyloxamic acid hydrazide [103] or by addition of (-)-ephedrine [104] to racemic (hexadienal) $\text{Fe}(\text{CO})_3$ complexes to give diastereomeric oxazolidines. Optically pure acyclic or

cyclic diene complexes have been used in asymmetric synthesis of cis- and trans-hemicaronic aldehydes [103] and of diene ethers and alcohols [17,18].

One of the most important applications of organometallic compounds in asymmetric synthesis is the use of chiral catalysts which effect asymmetric induction [105], e.g. production of L-DOPA using chiral rhodium catalysts in a catalytic asymmetric hydrogenation [106]. Iron porphyrins with optically active substituents have been used in asymmetric epoxidation of prochiral olefins in optical yields of up to 51% ee [107].

3. APPLICATION OF (DIENE)Fe(CO)₃ COMPLEXES IN POLYENE SYNTHESIS

3.1 Introduction

The formation of double bonds, preferably in a stereoselective way is of central interest in natural product synthesis of carotenes, insect pheromones, leukotrienes and antibiotics. This chapter contains the results of highly stereoselective reactions of functionalized dienes complexed to iron.

3.2 Synthesis of (5-8- η - β -Ionol)Fe(CO)₃ (58a) and (58b)

The β -ionone complex 57 is available in yields of more than 80% from the reaction of β -ionone and Fe₂(CO)₉ in ether [108]. This makes it a useful precursor for the synthesis of complexed vitamin A and carotene intermediates¹. The reduction of (5-8- η - β -ionone)Fe(CO)₃ 57 with sodium borohydride in methanol/water gave an interesting result. As β -ionone is an unsymmetrical diene it is also prochiral and complexation to a Fe(CO)₃ group therefore yields a chiral molecule. Reduction of the ketone to a secondary alcohol introduces a new chiral centre at C(9) and so two diastereomeric products were expected. However, the reduction produces only one product 58a which suggests, that the hydride attacks the ketone from the face anti to the metal. To test this prediction β -ionol 59 was complexed using Fe₂(CO)₉ and two diastereomeric products 58a and 58b (1:1) were isolated and characterized (Fig. 24). One of these had the same spectroscopic data as the product obtained from the reduction, while the other product had slightly different ¹³C-chemical shifts for the complexed diene system. This supports the assumption that a

1. Numbering of carbon skeleton in this chapter according to carotenoid convention.

diastereoselective reduction of a complexed unsaturated ketone can be carried out using sodium borohydride. In addition to attack from the face opposite the $\text{Fe}(\text{CO})_3$ group, one of the two possible rotamers (s-cis or s-trans) of the C(8)-C(9) bond must be predominantly populated. Evidence from force field calculations and ^1H NOE experiments [109] shows that the s-cis form is preferred. The extension of this method to enantiomerically pure complexed ketones would allow, after decomplexation, the enantioselective production of secondary alcohols. In particular, the use of this method in the synthesis of optically active carotene end-groups, such as commercially important zeaxanthin, could be promising.

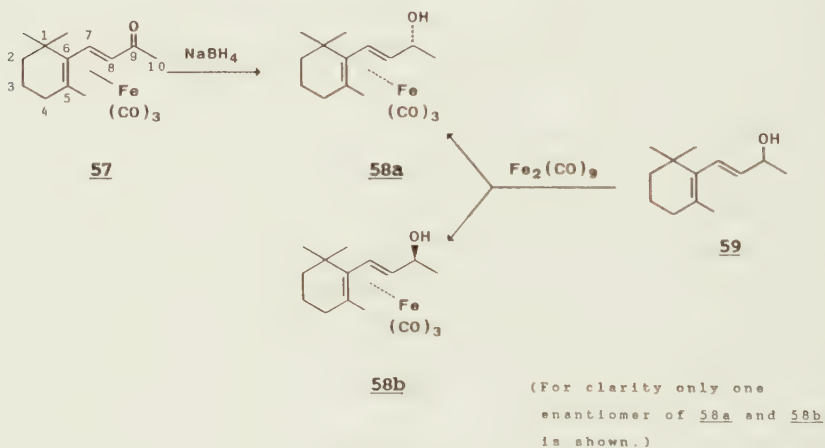


Figure 24

3.3 Synthesis of (7-10- η - β -Ionylideneacetonitrile) $\text{Fe}(\text{CO})_3$ 60 and (7-10- η - β -Ionylideneacetaldehyde) $\text{Fe}(\text{CO})_3$ 61

Aldol condensations of α,β -unsaturated aldehydes such as 2,4-hexadienal or 2-butenal have only a limited use in the synthesis of polyene chains as self-condensation reactions leading to

polymeric products reduce yields. Hafner et al. [110,111] have shown that the coordination of 2,4-hexadienal to $\text{Fe}(\text{CO})_3$ changes the reactivity of the diene system. The complex is insensitive to heat and base and undergoes neither self-condensation nor Michael addition due to fixation of the π -system and reduced conjugation with the functional group. Furthermore, this synthon can be employed in a chain elongation reaction sequence which permits diastereoselective synthesis of polyenes. A number of carbanions cleanly add to the aldehyde to give, after condensation polyene products extended by one double bond. A novel feature of this reaction is the fact that in some cases the $\text{Fe}(\text{CO})_3$ group experiences a 1,3-shift and effects a uniform reaction course with a diastereoselective formation of the newly formed double bond. This migration of the protecting group depends on the carbanions employed and the reaction time.

We attempted to extend this method to the synthesis of the carbon skeleton of carotenoid intermediates. In the reaction of two equivalents of acetonitrile with two equivalents of *n*-butyllithium at -78°C the white LiCH_2CN salt precipitates after about 30 minutes. The addition of one equivalent of (5-8- η - β -ionone) $\text{Fe}(\text{CO})_3$ **57** gives the C_{15} -nitrile **60** in 88% yield. This nitrile can be reduced with DIBAH to give the C_{15} -aldehyde **61** in 90% yield (Fig. 25).

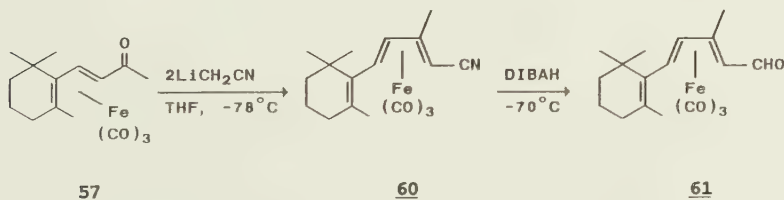
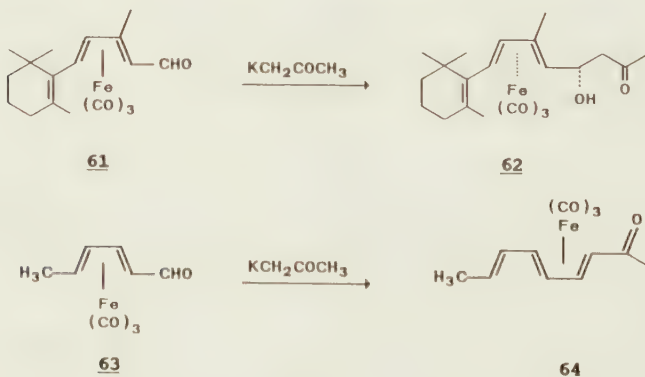


Figure 25

All additions of the LiCH_2CN to the β -ionone complex **57** resulted in migration of the $\text{Fe}(\text{CO})_3$ group. This is probably due to the endo methyl group at C(5) of the β -ionone complex which is distorted out of the diene plane by the protecting group. This facilitates migration as the methyl group can move back into the plane of the diene when the iron moiety shifts. To extend the polyene chain we attempted to add acetone to the C_{15} -aldehyde. Various procedures were employed but only the aldol addition product **62** was isolated (Fig. 26). This is in contrast to the addition of acetone to (hexadienal) $\text{Fe}(\text{CO})_3$ **63** where the migrated product and the non-migrated product were isolated [110]. Attempts to dehydrate **62** were unsuccessful. The best system for the deprotonation of acetone was potassium triphenylmethane which is a non-nucleophilic base [112]. Deprotonation of acetone gives the corresponding anion which on addition to the hexadienal complex **63** results in clean condensation and 100% concomitant migration of the iron moiety to give **64** (Fig. 26). The addition of the same reagent to the C_{15} -aldehyde complexes gives only the aldol product. The reason for the different reactivity between these two complexes remains unclear.



(Only one enantiomer of **62** is shown)

Figure 26

We have however managed to extend the polyene chain selectively by a second addition of the acetonitrile anion to the C_{15} -aldehyde complex which gave the C_{17} -nitrile complex **65** in 76% yield (Fig. 27). No migration product could be observed, but the newly formed double bond has (E)-configuration shown by the large H,H coupling of 15.6 Hz between H-C(11) and H-C(12).

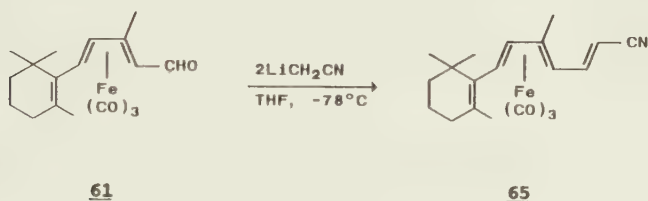


Figure 27

The extension of the polyene chain by one double bond produces a new diene system into which the $\text{Fe}(\text{CO})_3$ group could migrate. However, this new diene system also contains an endo methyl group at C(9) which may sterically interact with the iron moiety and prevent migration. From the reaction of optically pure hexadienal complex we know that the migration of the $\text{Fe}(\text{CO})_3$ can be formulated as a suprafacial migration. Previous experiments suggest that the migration of the protecting group is base-catalyzed and kinetically controlled. Thermodynamic control can be eliminated as Whitlock et al. [113] have reported that the thermal migration of the $\text{Fe}(\text{CO})_3$ group along unsubstituted polyene chains needs temperatures of more than 100°C . We believe that in the transition state the unfavourable steric interaction of the methyl substituent with the migrating group could be the explanation for this result.

TABLE 1

 ^1H CHEMICAL SHIFTS OF (IONYLIDENE) $\text{Fe}(\text{CO})_3$ COMPLEXES IN CDCl_3

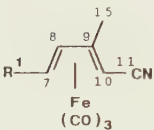
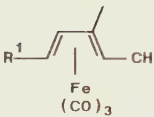
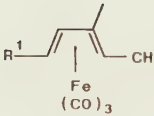
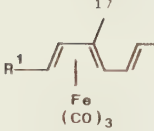
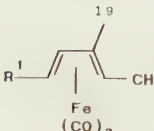
Compound	H(7)	H(8)	H(10)	H(11)	H(15)
 <u>60</u>	2.04	5.87	0.49	—	2.50
 <u>61</u>	2.41	5.77	1.16	9.45	2.55
 <u>92</u>	1.82	5.69	1.0	3.8	2.30
 <u>65</u>	2.17	5.74	1.03	6.78	H(17) 2.39
 <u>66</u>	1.73	5.74	1.02	3.75	H(19) 2.23
 $\text{R}^1 =$					
$\text{R}^2 = n\text{-C}_4\text{H}_9$					
(δ ^1H in ppm relative to TMS)					

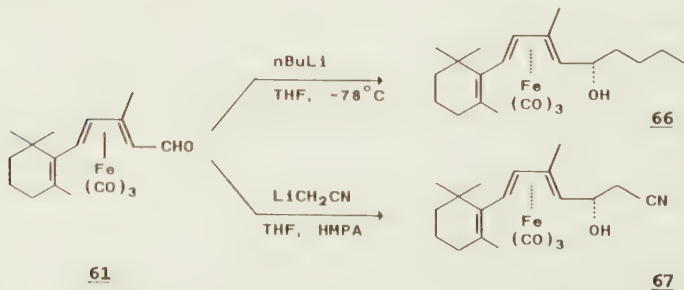
Table 2

¹³C CHEMICAL SHIFTS OF (IONYLIDENE)Fe(CO)₃ COMPLEXES IN CDCl₃

Compound	C(7)	C(8)	C(9)	C(10)	C(11)	C(15)	CO
60	64.9	87.4	95.6	25.4	a)	22.9	209.1
61	65.5	88.6	97.9	56.2	194.8	23.0	209.9
92	62.3	85.5	97.3	59.0	61.6	22.9	212.3
65	63.4	86.4	96.5	59.6	152.4	23.0	211.2
66	62.7 [*]	84.8	95.5	68.4 [*]	71.9 [*]	22.7	212.6
¹ R = ² R = n-C₄H₉ (δ ¹³C in ppm relative to TMS) (δ^* can be interchanged) (a) not observed)							

In conclusion, we can state that this polyene chain extension reaction can be usefully employed using LiCH_2CN as the reagent. It is however of limited use where the polyene chain contains a methyl group which could interfere with the migration mechanism. A diastereoselective two-step reaction in 76% overall yield of (7-10- η - β -ionylideneacetaldehyde) $\text{Fe}(\text{CO})_3$ **61** has been achieved. Conventional Wittig-Horner reaction of β -ionone with triethylphosphono acetate followed by reduction to the alcohol and manganese dioxide oxidation to the aldehyde proceeds in a non-stereospecific reaction in 55% overall yield [114].

In the course of our investigations of the condensation reactions of (7-10- η - β -ionylideneacetaldehyde) $\text{Fe}(\text{CO})_3$ we added a number of nucleophiles to this complex (Fig. 28). In all cases only one diastereomeric alcohol was isolated which confirms previous findings [17] that nucleophiles attack the carbonyl group from the face opposite the $\text{Fe}(\text{CO})_3$ group. In addition, the carbonyl group must be in a stable conformation, which implies that only one of the two possible rotamers (s-cis or s-trans) of the C(10)-C(11) single bond is populated. Proton NMR spectra show that at temperatures below -50°C complexed aldehydes prefer the s-trans conformation.



(Only one enantiomer of **66** and **67** is shown)

Figure 28

It is interesting to note that the carbonyl group of complexed ketones prefers the s-cis conformation. The steric interaction of the ketone methyl group with the vicinal proton on the diene is larger than for an aldehyde proton. The addition of n-BuLi, $\text{KCH}_2\text{COCH}_3$ and LiCH_2CN gave 66, 62 and 67 (intermediate of 65), respectively. Using optically active aldehydes this reaction has been employed in the synthesis of optically active secondary alcohols [104].

3.4 Synthesis and Reactions of Complexed Wittig-Horner Synthons

3.4.1 Synthesis of Bifunctionalized Diene Compounds

Previous investigations have shown that complexed acyclic diene systems of type 63 can be used in highly stereoselective Wittig and Wittig-Horner reactions [115].

To determine the scope of these reactions in polyene natural product synthesis we synthesized and complexed a number of bifunctionalized isoprene compounds.

(E)-4-Acetoxy-2-methyl-2-butenal² 68 [116] underwent a smooth Wittig-Horner reaction with triethyl phosphonoacetate to give the C₇-acetoxy ester 69 (Fig. 29). Selective base-catalyzed ester hydrolysis gave the C₇-alcohol ester 70, which was oxidized with manganese dioxide to give ethyl-6-oxo-4-methylhexa-2,4-dienoate 71. The alcohol ester 70 when treated with phosphorous tribromide gave the bromoester 72 which was converted in a Michaelis-Arbusow reaction to the C₇-phosphonate 73 by refluxing in triethyl phosphite [117, 117a].

2. We would like to thank BASF, Ludwigshafen for a generous gift of (E)-4-acetoxy-2-methyl-2-butenal 68.

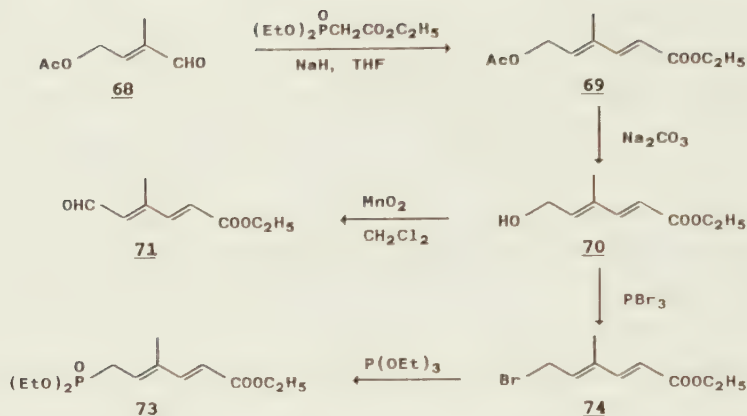


Figure 29

The C_7 -diester **75** was synthesized analogously from ethyl-4-oxo-3-methyl-2-butenate **74** and triethyl phosphonoacetate (Fig. 30).

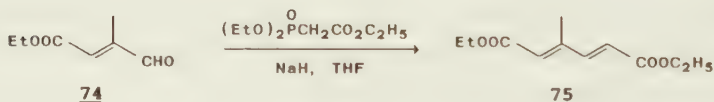


Figure 30

We synthesized the unsaturated C_7 -aldehydic ester³ **78** starting from ethyl- β -formylcrotonate. Its diethyl acetal **76** was condensed with ethyl vinyl ether in the presence of boron trifluoride etherate yielding the triethoxy ester **77** which was hydrolysed with *p*-toluenesulphonic acid (Fig. 31) [118].

3. We would like to thank F. Hoffmann-La Roche & Co. AG, Basle for a generous gift of **78**.

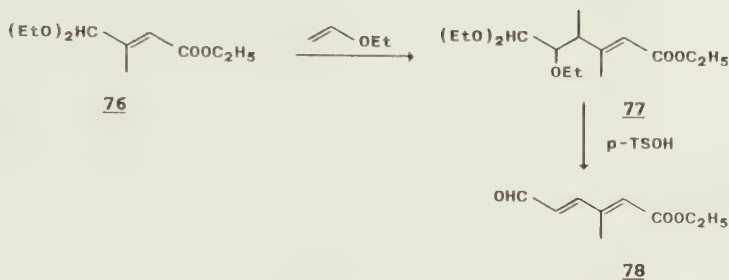


Figure 31

3.4.2 Complexation of Bifunctionalized Diene Compounds

Complexation of these dienes was accomplished by refluxing in ether with 1.5 equivalents of $\text{Fe}_2(\text{CO})_9$. Higher yields have been achieved by stirring the reaction mixture at room temperature for one hour before heating. If any starting material could still be detected after three hours, a further equivalent of $\text{Fe}_2(\text{CO})_9$ was added. A complete conversion is shown by the dark green colour of the mixture. Yields of the reaction depend also to a large extent on the diene employed. These differences are due in part to steric interactions and to electronic effects of the substituents of the diene. Thus, endo-substituted diene complexes give much lower yields on complexation than corresponding exo-substituted dienes irrespective of the substituents involved [119]. Furthermore, the type of substituents on the diene affects the complexation and thereby determines the yield. Yields of complexations of differently substituted dienes have shown the following trends : $\text{COOR} > \text{CHO} > \text{CH}_2\text{OAc} \gg \text{CN}$.

In particular, nitriles have given poor yields in complexation reactions, which could be explained by the much higher electron-withdrawing properties of this substituent leading to an electron deficient diene system which in turn hinders complexation. Further evidence is found in ^{57}Fe chemical shifts of nitrile complexes, which are deshielded by 200 ppm from corresponding ester and aldehyde complexes. Yields of these complexation reactions range from 65% for the acetoxyster **89** to 85% for the diester **90**.

3.4.3 The Wittig Reaction

In the Wittig reaction, an aldehyde or ketone is treated with a phosphorous ylide, prepared by reaction of a phosphonium salt with a base, to give an olefin. This reaction sequence is particularly useful, as the position of the newly formed carbon-carbon double bond is predictable and reaction stereochemistry can be controlled by the type of ylide used and by the reaction conditions. For example, non-stabilized phosphorous ylides react with aldehydes to give largely (Z)-alkenes, stabilized ylides give predominantly (E)-alkenes, and semi-stabilized ylides give 50:50 (Z/E)-mixtures (Fig. 32).

The mechanism of the reaction can be formulated as follows : The ylide reacts with the aldehyde to afford two dipolar betaine intermediates which collapse to (Z)- and (E)-alkenes and phosphine oxide via an oxaphosphetane species. NMR studies by Vedejs and co-workers [120] indicate that oxaphosphetanes are more important than betaines. A cis-oxaphosphetane gives the (Z)-alkene while a trans-oxaphosphetane gives the (E)-alkene. Bestmann [121] has proposed that oxaphosphetanes can open to zwitterions, which are free to rotate to the thermodynamically more stable threo isomer before decomposing to give (E)-

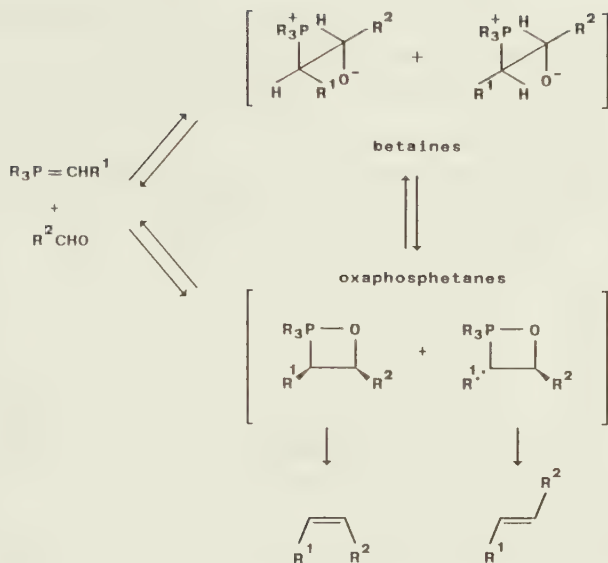


Figure 32

products. Stabilized ylides give more (E)-isomer which suggests that the zwitterion is longer lived as the anionic charge is stabilized. Schlosser [122] has speculated that cis-oxaphosphetanes are preferred with triphenylphosphorous ylides whereas trans-oxaphosphetanes are preferred with trialkyl phosphonium salts because of steric interactions between the phosphorous substituents and the approaching aldehyde.

Maryanoff and co-workers [123] have recently been able to directly observe individual diastereomeric oxaphosphetanes formed by reaction of non-stabilized ylides, using low temperature NMR spectroscopy. The authors report that the relative proportion of cis- and trans-oxaphosphetanes initially formed and the final proportion of (Z)- and (E)-alkene do not correspond. A greater amount of (E)-alkene is produced, which is

explained by a higher rate of reversal of the cis-oxaphosphetane to the ylide and aldehyde.

No betaines or oxaphosphetanes could be observed in reactions of semi-stabilized and stabilized phosphorous ylides. Thermodynamic control of the reaction, resulting predominantly in (E)-alkene formation, has been proposed but this remains speculative until intermediates have been trapped or detected.

The Wittig-Horner reaction uses ylides prepared from phosphonates, and this method has two main advantages. Firstly, these ylides are more reactive than corresponding phosphoranes and can also react with ketones and secondly, a phosphate ester is formed, which unlike triphenylphosphine oxide is soluble in water thus making it easier to separate from the product.

3.4.4 New Contributions to Wittig and Wittig-Horner Reactions using Organoiron Compounds

Addition of tertiary phosphanes and phosphites to cationic iron complexes give metal coordinated phosphonium salts and phosphonates which have been used in Wittig and Wittig-Horner reactions [115][124]. To investigate the synthetic utility of these reactions, we first reacted complexed aldehydes with uncomplexed ylides and then with complexed ylides.

3.4.5 Synthesis of (11-14- η -Vitamin A)Fe(CO)₃ (**81**)

The deprotonation of β -ionyltriphenylphosphonium bromide **79** was accomplished using potassium-*t*-butoxide (Fig. 33). The complexed aldehyde **80** was then added to this solution. The ester formed was reduced with DIBAL to give complexed vitamin A **81** in 64% overall yield relative to complexed aldehyde. To determine the configuration of the newly formed 9,10-carbon-carbon double bond

^1H - and ^{13}C -NMR was used. Eschenmoser [125] has reported that H-C(8) is shifted downfield by approximately 0.5ppm in (9Z)-isomers of carotenes.

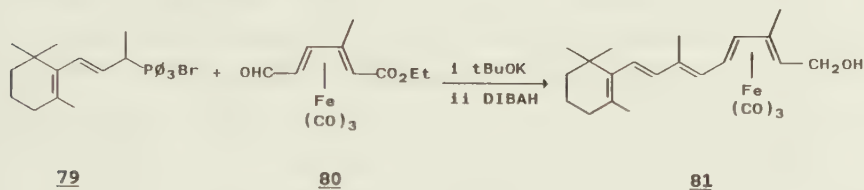


Figure 33

This result has been confirmed in NMR studies [126] of (9Z)-vitamin A derivatives and (9Z)-carotenes. The ^1H -shifts of "in-chain" methyl groups are very poor indicators for the position of the (Z)-double bond. However, the ^{13}C chemical shifts of a methyl group attached to a (Z)-double bond is considerably shifted downfield, from 12 ppm for the E-isomer to around 20 ppm for the Z-isomer [127]. The complexed vitamin A has a signal for H-C(8) at 6.13 ppm and a signal at 12.6 ppm for C(19). This data suggests that the newly formed double bond has (E)-configuration and confirms previous findings that the use of potassium-t-butoxides as the base in Wittig reactions of complexed aldehydes and complexed phosphonium salts gives the (E)-isomer. Birch and co-workers [127a] have reacted retinal with $\text{Fe}_3(\text{CO})_{12}$ to give (11-14- η -retinal)- $\text{Fe}(\text{CO})_3$. X-ray analysis of this compound confirmed the position of the iron group. The position of addition is readily rationalized by the necessary cisoid and planar configuration of the chain at the position where $\text{Fe}(\text{CO})_3$ is added. Other possible positions lead to less flexible chains in the products.

3.4.6 Synthesis of Complexed C₁₄-Polyenes

In order to achieve the stereoselective coupling of two complexed diene synthons in a Wittig-Horner reaction we chose to add the C₇-phosphonate ester **73** to the complexed C₇-aldehydic ester **82** (Fig. 34). Deprotonation of the phosphonate at -78°C with n-butyllithium and subsequent addition of the iron complex **82**, gave the mono-complexed C₁₄-diester **83** in 84% yield. The (H,H) coupling constant between H-C(6) and H-C(7) is 15.6 Hz which suggests (E)-configuration for the newly formed double bond.

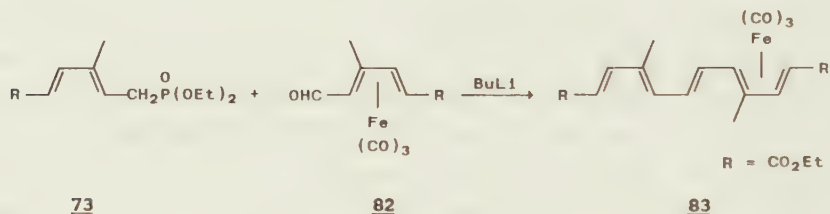


Figure 34

The reaction of complexed C₇-aldehyde ester **82** with complexed C₇-phosphonate ester **84** proceeded smoothly to give the bis-complexed C₁₄-diester **85** in 85% yield (Fig. 35). The protons H-C(5), H-C(5'), H-C(6) and H-C(6') form a higher order AA'XX' spin system. High resolution 400 MHz ¹H-NMR resolved all the necessary lines to fully analyze the system. Using the PANIC (Bruker) simulation and iteration program a value of 14.6 Hz for the coupling between H-C(6) and H-C(6') was determined. This coupling is slightly smaller than the one determined for the mono-complexed product, but an (E)-configuration can still be proposed. Reduction of the diester **85** gave the bis-complexed C₁₄-diol **86** in 90% yield. The coupling for the central double bond was again determined by iterative methods. Although the

coupling is slightly reduced (14.4 Hz) the configuration has most probably remained unchanged.

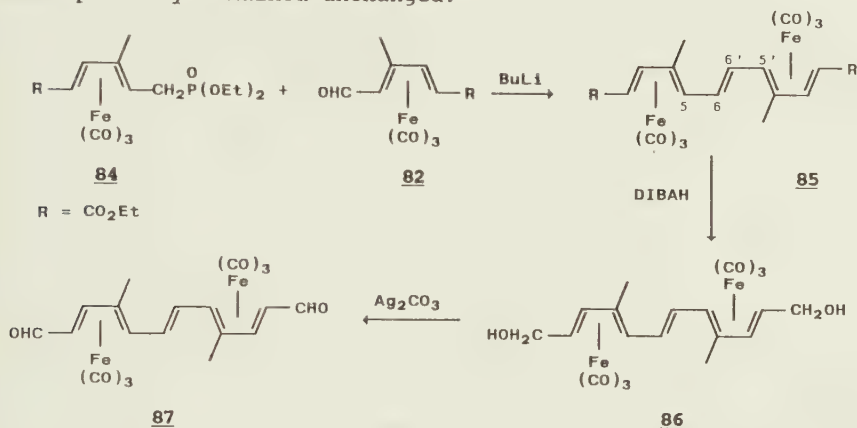


Figure 35

Few useful methods for oxidizing functional groups attached to iron tricarbonyl complexes have been reported. The oxidizing power of most reagents is not limited to the functional group and therefore decomplexation reactions occur. Reagents such as pyridinium dichromate and activated dimethyl sulfoxide gave poor and irreproducible results in our hands. The reaction of silver nitrate in a slurry of Celite and sodium carbonate in water gives adsorption of silver carbonate on Celite. Treatment of complexed alcohols with this reagent gave isolated yields of between 50-70% depending on the substrate. The bis-complexed diol **86** was oxidized to give the C_{14} -dial **87** in 56% yield (Fig. 35).

The C_{15} -aldehyde **61** reacted with the ylide from **73** to give monocomplexed C_{22} -ester **88** (Fig. 36). This reaction also proceeded stereospecifically to give (E)-configuration at the newly formed double bond.

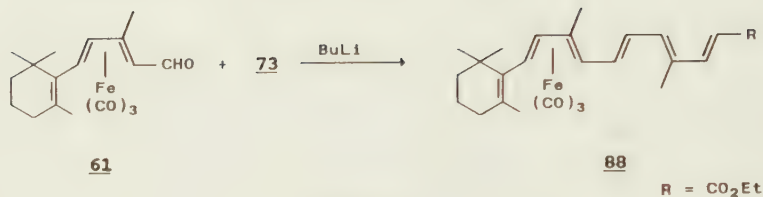


Figure 36

3.4.7 Discussion

Three dinuclear iron complexes **85**, **86** and **87** have been synthesized. From spectroscopic evidence the relative position of the two $\text{Fe}(\text{CO})_3$ groups cannot be determined. The two protecting groups could be attached to the same face (chiral-form) or to opposite faces of the polyene (meso-form). From X-ray data of a similar (E)- C_{12} -polyene we know that the $\text{Fe}(\text{CO})_3$ groups are coordinated to opposite sides of the polyene [115]. These results show that the application of (diene) $\text{Fe}(\text{CO})_3$ synthons in polyene synthesis allows highly stereoselective formation of (E)-double bonds to be carried out. This high selectivity could be explained by steric interactions between the $\text{Fe}(\text{CO})_3$ group complexed to the aldehyde and the phosphonate. The ylide approaches the aldehyde from the face opposite to the $\text{Fe}(\text{CO})_3$ group **A** (Fig. 36a). The diene part of the phosphonate orients itself so that a trans-oxaphosphetane **B** is formed. This trans-oxaphosphetane leads after elimination of the phosphate ester to the formation of an (E)-alkene **C**. The fact that reactions of uncomplexed phosphonate with complexed aldehydes give only the (E)-isomer suggests that the second $\text{Fe}(\text{CO})_3$ group is not involved in this steric interaction. These assumptions are based solely on a molecular model of a possible interaction

between the $\text{Fe}(\text{CO})_3$ group of the aldehyde and the phosphonate. Further investigations are necessary to determine the reasons for this selectivity. The effect of the base employed in the ylide generation remains unclear. In addition, it has been shown that functionalized polyenes can be stabilized by complexation to an $\text{Fe}(\text{CO})_3$ group. For the successful application of these reactions to polyene synthesis an efficient decomplexation method is essential. A number of mild oxidation reactions have been described in literature (see Chapter 2.7). In particular, care has to be taken that functional groups present in the molecule survive the decomplexation conditions. In our experience best results were achieved with ceric ammonium nitrate in the two-phase acetonitrile/pentane solvent system. Complexed nitriles, ketones and aldehydes have been decomplexed to give the free polyenes in yields of between 85-95% [110].

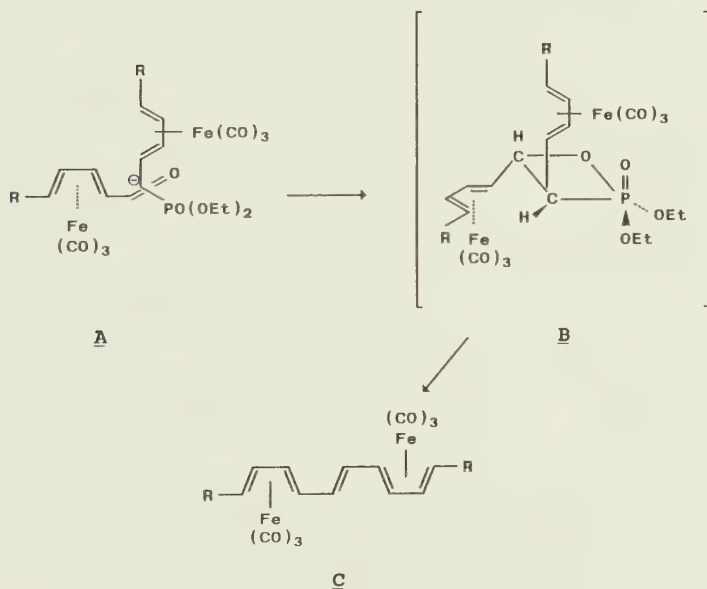


Figure 36a

4. CARBONYL LIGAND EXCHANGE REACTIONS IN (DIENE)Fe(CO)₃- AND (ENONE)Fe(CO)₃ COMPLEXES

4.1 Introduction

The iron tricarbonyl moiety has been shown (see Chapter 2) to act as a protecting and stabilizing group which can be used to modify the reactivity of diene systems.

The replacement of one or more carbon monoxide molecules by η^2 -ligands such as phosphanes, phosphites or isonitriles alters the electron density at the metal and thereby also influences the reactivity of the organic ligand. Replacement of carbon monoxide by triphenylphosphane in (cyclohexa-1,3-diene)Fe(CO)₃ increases the nucleophilic character of the diene which facilitates Friedel-Crafts acylation [73]. It also decreases the electrophilic character of the derived dienyl cationic salt [128]. In addition, a further feature of carbon monoxide substitution by an optically active phosphane ligand is the potential for asymmetric induction. This has recently been demonstrated in one case by the addition of a cyanide ion to (C₆H₇)Fe(CO)₂PPh₂ (neomenthyl) **93** (Fig. 37) [129].

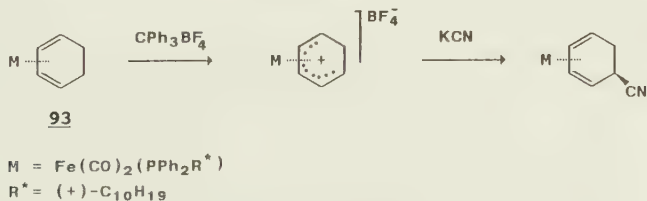


Figure 37

For the application of phosphorous substituted (diene) $\text{Fe}(\text{CO})_2\text{L}$ complexes an efficient method is required.

Previous methods included :

- a) Irradiation of the (diene) $\text{Fe}(\text{CO})_3$ complex in the presence of a η^2 -ligand in inert aprotic solvents such as benzene, hexane or cyclohexane [130,131];
- b) Thermal substitution by heating (diene) $\text{Fe}(\text{CO})_3$ complexes with η^2 -L (L = phosphane, phosphite etc.) in sealed tubes at elevated temperatures, and thermal substitution by refluxing (diene) $\text{Fe}(\text{CO})_3$ complexes with η^2 -L in high boiling solvents such as cyclohexanol, benzene and toluene [133,134,135,136].
- c) Transfer of the iron moiety by a photolysis reaction of $\text{R}_3\text{PFe}(\text{CO})_4$ and the diene [129] or by employing ((E)-4-phenyl-3-buten-2-one) $\text{Fe}(\text{CO})_2\text{PR}_3$ as the transfer agent [136].

These methods all have inherent disadvantages, which is why not many applications of (diene) $\text{Fe}(\text{CO})_2\text{L}$ complexes in organic synthesis have been reported.

Prolonged irradiation (method a) proceeds in low yields and leads in most cases to decomplexation and formation of $\text{Fe}(\text{CO})_3(\text{PR}_3)_2$. The mono-substituted complex can also react further to yield the bis-substituted complex (diene) $\text{Fe}(\text{CO})\text{L}_2$ and thereby reduces an already low yield even further. Yields for the thermal methods are much higher (40-60%), particularly benzene has proved to be a useful solvent. However, the exchange of a second carbon monoxide has also been reported. Transfer using $\text{Fe}(\text{CO})_4\text{PR}_3$ appears suitable for unsubstituted

(cyclohexa-1,3-diene)Fe(CO)₃ complexes but low yields (15%) have been reported for functionalized complexes such as (2-methoxycyclohexa-1,3-diene)Fe(CO)₃ complexes [135].

The transfer of an Fe(CO)₂PR₃ moiety from (enone)Fe(CO)₂PR₃ complex requires a rigid s-cis conjugated diene which is often not accessible.

Metal carbonyl complexes have been known to react with a number of aliphatic, aromatic and heterocyclic amine oxides in a deoxygenation reaction to yield the corresponding amines [137]. It has been shown that one mole of carbon dioxide is formed for every mole of pyridine-N-oxide deoxygenated. Shvo and Hazum [31] have reported a simple synthesis in moderate to good yields of (diene)Fe(CO)₃ complexes by using amine oxides to promote complexation. Oxidation of the carbon monoxide ligand takes place and an unsaturated organometallic moiety (Fe(CO)₄) is generated which can coordinate to the diene. Some studies of the reaction mechanism have appeared in literature, which propose that on reaction of Fe(CO)₅ with trimethylamine oxide at low temperature in THF, carbon dioxide evolves and the free amine coordinates to the metal to form Fe(CO)₄N(CH₃)₃ **7** [138] (Fig.38). Kelly and Birch [139] have recently reported that (cyclohexadiene)Fe(CO)₃ complexes react with (CH₃)₃NO in the presence of P(Ph)₃ in boiling acetone to give the corresponding (cyclohexadiene)Fe(CO)₂(P(Ph)₃) complexes.

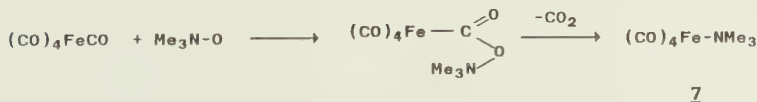


Figure 38

Not all carbonyl ligands are susceptible to attack by trimethylamine oxide. Empirical studies indicate that there is a reasonable correlation between the reactivity of the metal carbonyl towards trimethylamine oxide and the stretching force constant (CO-bond) based on a simple energy-factor force [140,141]. A correlation between $\nu(\text{CO})$ and the reaction conditions has been proposed. Consequently, Koelle [141], Brown and co-workers [140] concluded that a stretching frequency $\nu(\text{CO}) > 2000 \text{ cm}^{-1}$ is a useful guideline for predicting whether or not an amine oxide reagent will react with a given substrate.

Gladysz and co-workers [142] have demonstrated the utility of trimethylamine oxide for decarbonylation of arylmanganese compounds which were not amenable to photochemical or thermal methods. Substitution reactions of $\text{PhMn}(\text{CO})_5$ and $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$ complexes ($\text{M} = \text{Mo}$ and W ; $\text{X} = \text{halide}$) with phosphines and arsanes proceed rapidly at room temperature in the presence of trimethylamine oxide to give $\text{cis-PhMn}(\text{CO})_4\text{L}$ or $\text{cis-(}\eta^5\text{-C}_5\text{H}_5\text{)-M}(\text{CO})_2\text{LX}$, respectively [140]. Stereoselectivity, product yields and reaction rates are enhanced by the use of the amine oxide reagent.

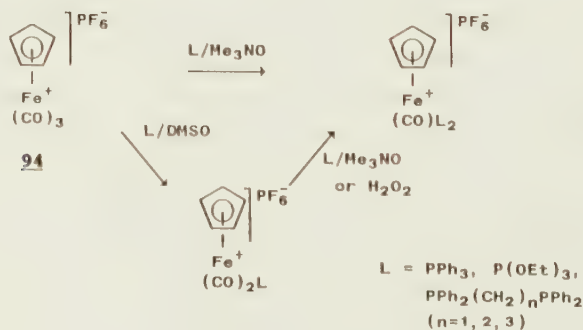


Figure 39

Replacement of carbon monoxide ligands in cationic organo-transition metal complexes by phosphane and phosphite ligands can also proceed efficiently. Davies [143] has shown that oxidative stepwise displacement in cationic iron complexes can be achieved by adding $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_3]^+\text{PF}_6^-$ **94** to a solution of phosphine in dimethyl sulphoxide (Fig. 39). Subsequent addition of this monosubstituted product to an acetone solution of phosphane ligand and trimethylamine oxide replaces a second carbon monoxide ligand by a phosphane.

Selective replacement of one carbon monoxide ligand of $\text{Ru}(\text{CO})_2\text{-X}_2\text{L}_2$ complexes **95** ($\text{X} = \text{Br}^-$ or CF_3COO^- ; $\text{L} = 1,10\text{-phenanthroline (phen)}, 2,2'\text{-bipyridyl (bpy)}$ or PPh_3) was achieved by the reaction with trimethylamine oxide in pyridine [144] (Fig. 40).

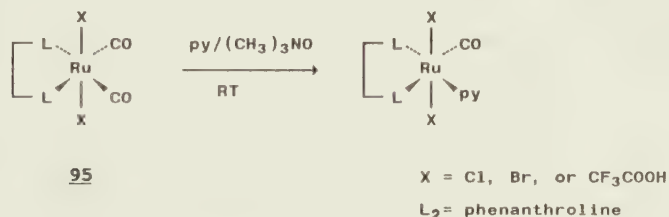


Figure 40

Substitution of only one carbon monoxide by pyridine occurs as the second carbon monoxide ligand has a stretching frequency in the region of 1940 cm^{-1} . This carbonyl group could not be removed even in boiling pyridine which is consistent with earlier observations. However, the same authors have reported that both carbonyl groups of $\text{Ru}(\text{CO})_2\text{Cl}_2\text{L}_2$ can be exchanged on reaction with bidentate ligands and trimethylamine oxide in boiling 2-methoxy-ethanol even though the reaction proceeds

through an intermediary monocarbonyl with $\nu(\text{CO}) < 2000 \text{ cm}^{-1}$ [145]. No decarbonylation was achieved in the absence of trimethylamine oxide.

4.2 Selective Decarbonylation of $(\text{Diene})\text{Fe}(\text{CO})_3^-$ and $(\text{Enone})\text{Fe}(\text{CO})_3$ Complexes with Concomitant Ligand Exchange

We envisaged a number of strategies to achieve selective decarbonylation of $(\text{diene})\text{Fe}(\text{CO})_3$ complexes. In particular, the use of oxidizing compounds or solvents was considered. Furthermore, we employed solvents capable of complexing metals which could coordinate and thereby stabilize unsaturated species. Carbon monoxide replacement by triethyl phosphite was attempted using the ligand as the solvent. The $(\text{butadiene})\text{Fe}(\text{CO})_3$ complex **96** was inert in this solvent and no decarbonylation occurred on addition of ceric ammonium nitrate or trimethylamine oxide. The addition of a small quantity of methanol initiated rapid evolution of carbon monoxide, but no product could be detected. The ceric salt was too powerful an oxidizing agent.

Therefore, trimethylamine oxide which had been successfully applied before was tried in combination with a ligand ($\eta^2\text{-L}$) in various solvents of which acetonitrile proved most useful. This solvent can coordinate well to metals and the work-up of the reaction was greatly facilitated (Fig. 41). The ratio complex/trimethylamine oxide/ligand is critical for the successful application of this method. Equimolar ratios gave incomplete conversion and decomposition. For complete reaction to take place (i.e. no starting material detectable) more than 1.5 equivalents of the oxidizing agent were required. If the ligand amount was below two equivalents decomposition occurred. Temperature dependence was also evident. For the butadiene and hexadienal complexes a temperature of 37°C gave the most

consistent results. Above 40°C decomposition products were formed.

Trimethylamine oxide is only partially soluble in acetonitrile and as the reaction proceeds, the solid slowly disappears. Thin-layer chromatography permits efficient monitoring of the reaction course and work-up is conveniently effected by the addition of hexane to the reaction mixture. A two-phase system hexane/acetonitrile is formed which is stirred and the apolar solvent containing all the product and excess ligand is collected. Yields can be improved by adding 10% ether to the hexane.

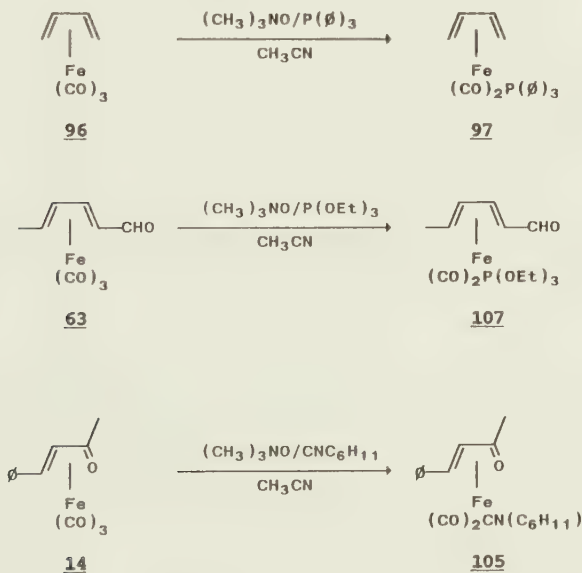


Figure 41

To show the versatility of the method it was applied to acyclic (diene)Fe(CO)₃, functionalized diene and heterodiene complexes. As a representative combination of η^2 -ligands the introduction of phosphanes, phosphites and isonitriles was attempted and achieved (Fig. 41).

The reaction time of (butadiene)Fe(CO)₃ **96**, ((Z)-pentadiene)-Fe(CO)₃ **97** and (hexadienal)Fe(CO)₃ **63** was between 3-5 hours at 37°C. The heterodiene complex **14** reacted within ten minutes at room temperature but better yields were achieved at 0°C. Yields of these reactions range from 60-93%, with triethylphosphane consistently producing yields in excess of 90%. The reaction is highly selective as only one carbon monoxide is replaced by a new ligand. No evidence for the formation of (diene)Fe(CO)L₂ could be found in any of the reactions. The $\nu(\text{CO})$ of all the products of type (diene)Fe(CO)₂L formed is below 2000 cm⁻¹ which confirms earlier findings that trimethylamine oxide attacks only carbon monoxide ligands with a stretching frequency higher than 2000 cm⁻¹.

One bidentate ligand, 1,2-bis(diphenylphosphino)ethylene, was used in a reaction with (hexadienal)Fe(CO)₃ **63** (Fig. 42). This ligand is sparingly soluble in acetonitrile and gave very low yields of the dimeric bridged compound **111** and a number of decomposition products.

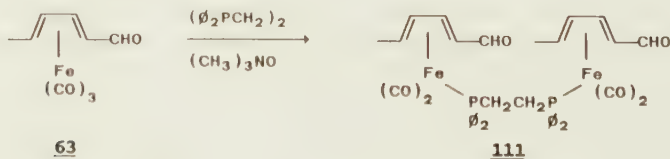


Figure 42

Attempts using the same method to exchange a second carbon monoxide ligand have so far proven unsuccessful. A number of different solvents and higher reaction temperatures were used but this lead to decomposition.

We have successfully synthesized the first iron diene complex with three different η^2 -ligands by irradiating a benzene solution of (hexadienal)Fe(CO)₂(P(OEt)₃) **107** in the presence of triethyl phosphane (Fig. 43).

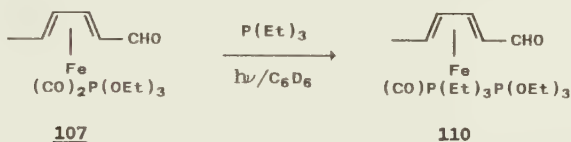


Figure 43

After overnight irradiation and subsequent chromatography, the product (hexadienal)Fe(CO)(P(OEt)₃)(P(Et)₃) **110** was isolated in 22% yield. ¹H-, ¹³C- and ³¹P-NMR showed that two isomers were present in a 10:1 ratio. Crystallization from hexane/ether 1/1 gave a pure sample of the major isomer. The structure elucidation was accomplished using X-ray diffraction analysis. The crystallographic data including space group, lattice parameters and the content of the asymmetric unit are listed in the experimental part (see Chapter 7.39). This is the first X-ray analysis of a (η^4 -diene) iron complex with three different η^2 -ligands.

The X-ray structure of **110** is shown in Figure 44a. A stereoscopic representation is shown in Figure 44b. From these

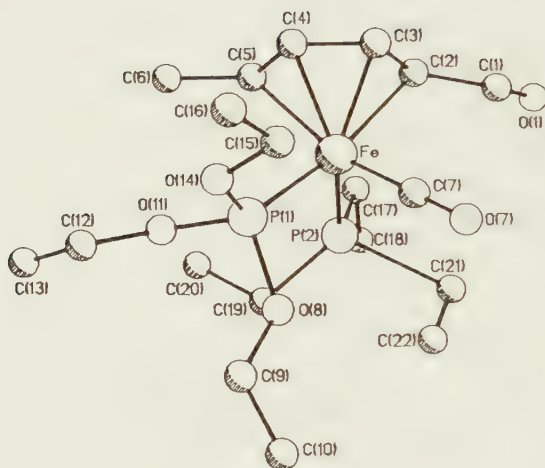


Fig. 44a X-ray structure of 110 with numbered atoms

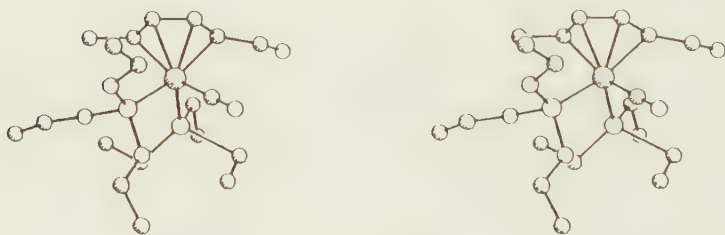


Fig. 44b Stereoscopic representation of 110

results the relative positions of the phosphorous substituents can be determined in the solid state. The P(Et)_3 ligand is in the apical position while the phosphite and the remaining carbon monoxide ligand occupy the two basal positions. In the ^{31}P -NMR spectrum of the product mixture a major and minor product can be identified. In both isomers two signals, one for phosphane and one for phosphite are observed. The two-bond (P,P) coupling for the major isomer was found to equal 38.0 Hz while the minor isomer had similar shifts for the two phosphorous ligands but only a coupling of 5.3 Hz for $^2J(\text{P,P})$. This isomer could have the two phosphorous ligands in basal position with the carbon monoxide ligand in apical position.

We have also shown that the $(\text{hexadienal})\text{Fe}(\text{CO})_2(\text{P(OEt)}_3)$ complex **107** can be reduced with sodium borohydride to give the alcohol complex **112** which in turn can be protonated to give $[(\text{hexadienyl})\text{Fe}(\text{CO})_2(\text{P(OEt)}_3)]^+\text{BF}_4^-$ **113** (Fig. 45).

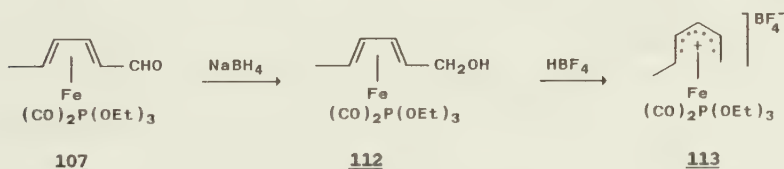


Figure 45

This ligand exchange method was also successfully applied to a cobalt complex, $\text{CpCo}(\text{CO})_2$, which gave decarbonylation and replacement by triethyl phosphite. The cyclopentadienyl ^{13}C signal is a doublet with a (P,C) coupling of 1.4 Hz and this confirms that only one carbonyl ligand has been exchanged.

4.3 Discussion of NMR Spectra

The ^{13}C chemical shifts of iron carbonyl groups adjacent to phosphorous and isonitrile ligands in (butadiene) $\text{Fe}(\text{CO})_2\text{L}$ complexes range between 216.3 and 217.7 ppm. This is a low field shift of about 5 ppm compared to the value found for (butadiene) $\text{Fe}(\text{CO})_3$. The chemical shifts of C(1) and C(2) in the diene ligand are also affected by the substitution of phosphorous and isonitrile for carbon monoxide. In general, there is a high field shift found for C(1) and C(2) of 1-2 ppm. Coupling between the phosphorous and carbonyl is found for all (butadiene) $\text{Fe}(\text{CO})_2\text{L}$ products and ranges from 12.0 Hz for $\text{L} = \text{P}(\text{Et})_3$ to 18.6 Hz for $\text{L} = \text{P}(\text{OEt})_3$. No coupling is found between the phosphorous ligand and the diene system in 97 and 98, but in 97 the phosphorous couples to C(1) of butadiene. Proton chemical shifts of the phosphorous substituted butadiene complexes are not affected to any large extent and differences range between 0.1 and 0.3 ppm. Substitution of isonitrile for carbon monoxide causes a downfield shift of 0.3 ppm and 0.2 ppm for $\text{H}-\text{C}(2)$ and $\text{H}_\beta-\text{C}(1)$, respectively.

Two carbonyl signals are found for complexes with unsymmetrical diene ligands such as Z-pentadiene and hexadienal. The two carbonyl groups are now diastereotopic and give rise to a signal each. For (Z-pentadiene) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ 101 chemical shifts of 216.2 and 216.5 have been determined and the phosphorous couplings are 19.0 Hz and 21.8 Hz. Only for the signal of C(4) has a (P,C) coupling been observed (3.6 Hz).

The spectra of the three phosphorous substituted hexadienal complexes 106, 107 and 108 also have two carbonyl signals both of which show a coupling to phosphorous. Only the signals for

C(2) and C(5) show a coupling to phosphorous (3.0-3.7 Hz). This general trend in these complexes suggests that the bonding between iron and the carbons C(2) and C(5) has more s-character than the bonding between iron and C(3) and C(4). The carbonyl shift of the aldehyde group is shifted downfield by substitution of carbon monoxide by a phosphorous ligand. Substitution of two carbon monoxide ligands by one phosphite and one phosphane (**110**) shifts the aldehyde carbonyl group from 195.7 to 198.3 ppm. Phosphorous couplings to C(2) and C(5) leads to double doublet signals for these carbons, while no coupling can be observed to C(3) and C(4). The signal for the remaining carbonyl group has not been observed.

These results suggest that the substitution of a carbonyl ligand by a phosphane, phosphite or isonitrile ligand probably influences the rotation, but at room temperature this process is still too fast for detection by NMR. To determine the preferred position of the new ligand and determine the dynamics of the rotation low temperature NMR experiments are necessary.

The ^1H -, ^{13}C -, and ^{31}P -NMR data of all the products formed are summarized in the Tables 3-8.

Table 3

 ^1H CHEMICAL SHIFTS OF (BUTADIENE) $\text{Fe}(\text{CO})_2\text{L}$ COMPLEXES IN C_6D_6

Compound	$\text{H}_\text{a}(1)$	$\text{H}_\text{b}(1)$	$\text{H}(2)$	$\text{H}(3)$	$\text{H}_\text{a}(4)$	$\text{H}_\text{b}(4)$	$\text{H}(\text{L})$
 $(\text{CO})_2\text{P}\phi_3$ <u>97</u>	0.0	1.47	4.93	4.93	0.0	1.47	7.60- 7.14
 $(\text{CO})_2\text{P}(\text{OEt})_3$ <u>98</u>	0.03	1.64	5.0	5.0	0.03	1.64	3.8 1.03
 $(\text{CO})_2\text{P}(\text{Et})_3$ <u>99</u>	0.35	1.36	4.89	4.89	0.35	1.36	1.20 0.74
 $(\text{CO})_2\text{CN}(\text{C}_6\text{H}_{11})$ <u>100</u>	0.1	1.54	5.07	5.07	0.1	1.54	2.79 1.26 1.08 0.92 0.82
 $(\text{CO})_2\text{P}(\text{OEt})_3$ <u>101</u>	1.44	1.82	5.12	5.01	-	2.62	1.11 (CH_3) 3.82 1.08

 $(\delta \text{ } ^1\text{H}$ in ppm relative to TMS)
$$\left[\text{Proton assignment} = \begin{array}{c} \text{H}_\text{b} \\ \text{H}_\text{a} \end{array} \begin{array}{c} \diagup \quad \diagdown \\ | \quad | \\ \diagdown \quad \diagup \end{array} \right]$$

Table 4

 ^{13}C AND ^{31}P CHEMICAL SHIFTS OF (BUTADIENE) $\text{Fe}(\text{CO})_2\text{L}$ COMPLEXES IN C_6D_6

Compound	C(1)	(C2)	P(R) ₃	CO	³¹ P
 (CO) ₂ Pφ ₃ <u>97</u>	40.8	84.4	136.0 133.1 129.5 128.0	217.7	73.5
 (CO) ₂ P(OEt) ₃ <u>98</u>	39.5	84.0	60.4 16.4	216.3	182.3
 (CO) ₂ P(Et) ₃ <u>99</u>	38.3	83.5	21.0	217.4	53.9
 (CO) ₂ CN(C ₆ H ₁₁) <u>100</u>	38.3	84.6	157.0 51.3 32.9 25.2 22.9	216.9	–
	C(1)	C(2)/C(3)	C(4)		
 (CO) ₂ P(OEt) ₃ <u>101</u>	39.2	86.2/88.5	49.9	13.4 (CH ₃) 59.9 16.1	216.5 216.2 178.7

(δ ^{13}C in ppm relative to TMS; δ ^{31}P in ppm relative to H_3PO_4 (external))

Table 5

 ^1H CHEMICAL SHIFTS OF (BDA)Fe(CO) $_2$ L COMPLEXES

Compound	H(1)	H(3)	H(4)	Ph	H(L)
 Fe (CO) $_2$ Pφ $_3$ <u>102</u>	2.48	5.77	1.97	7.41- 7.08	6.61
 Fe (CO) $_2$ P(OEt) $_3$ <u>103</u>	2.28	5.49	2.90	7.33 7.11 6.99	3.89 1.04
 Fe (CO) $_2$ (CNC $_6$ H $_{11}$) <u>104</u>	2.46	5.13	4.15	7.40 7.09 6.93	3.0-3.2 1.4- 1.1 1.0- 0.8
 Fe (CO) $_2$ (CNCH $_2$ CO $_2$ Et) <u>105</u>	2.50	5.84	4.50	7.40- 7.09	4.30 2.2 1.32

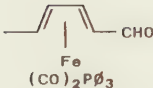
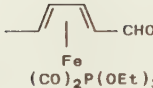
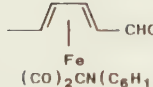
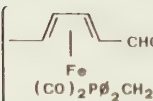
(δ ^1H in ppm relative to TMS)

Compound	C(1)	C(2)	C(3)	C(4)	Ph	C(L)	Co	³¹ P
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(δ ^{13}C in ppm relative to TMS; δ ^{31}P in ppm relative to H_3PO_4 (external))
(a) not observed, * signals interchangeable)

Table 7

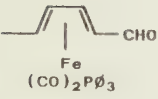
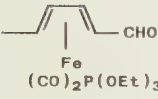
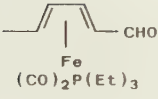
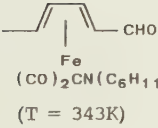
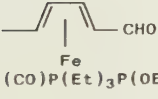
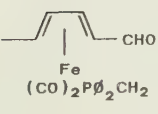
 ^1H CHEMICAL SHIFTS OF (HEXADIENAL)Fe(CO) $_2$ L COMPLEXES IN C_6D_6

Compound	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(L)
 <u>106</u>	9.1	0.17	5.31	4.62	0.17	1.06	7.6 7.04 0.94
 <u>107</u>	9.23	0.91	5.20	4.63	1.12	1.32	3.83 1.04
 <u>108</u>	9.05	*0.63 0.69	5.06	4.47	*0.69 0.63	1.17	1.47 0.78
 <u>109</u>	9.28	0.86	5.43	4.69	0.98	1.22	2.97 1.4- 1.1 1.0- 0.9
 <u>110</u>	9.51	0.37	5.11	4.63	0.79	1.43	3.60 1.06 1.85 0.97
 <u>111</u>	9.07	0.25	5.15	4.45	0.05	0.85	7.6- 7.2 7.1- 6.9 2.52

(δ ^1H in ppm relative to TMS, *signals interchangeable)

Table 8

 ^{13}C CHEMICAL SHIFTS OF (HEXADIENAL) $\text{Fe}(\text{CO})_2\text{L}$ COMPLEXES IN C_6D_6

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(L)	CO
 <u>106</u>	196.3	59.8/ 60.9	82.7	89.9	60.9/ 59.8	17.9	135.7 132.9 -127.0	214.9 211.6
 <u>107</u>	196.5	56.9/ 58.4	81.7	89.1	58.4/ 56.9	18.8	61.1 16.3	213.6 211.5
 <u>108</u>	196.8	53.9 56.6	81.8	88.7	56.3 53.9	19.2	20.5 7.8	215.4 212.2
 <u>109</u>	195.1	54.4/ 55.4	80.4	88.9	55.4/ 54.4	18.9	160.3 54.9 32.9 25.0 23.0	215.4 214.6
 <u>110</u>	198.3	54.6/ 53.0	75.6	88.9	53.0/ 54.6	19.1	60.7 16.1	-
 <u>111</u>	197.8	58.5/ 60.26	82.4	90.2	60.3/ 58.5	18.0	133.6 132.1 130.0	213.9 211.1

(δ ^{13}C in ppm relative to TMS)

5. NUCLEOPHILIC ADDITIONS TO CATIONIC IRON COMPLEXES

5.1 Introduction

The ability of certain highly reactive carbenium ions (e.g. $C_6H_7^+$, $C_7H_7^+$, $C_7H_9^+$ etc.) to be stabilized by metal coordination has greatly facilitated the investigation of their electrophilic chemistry. The most thoroughly researched stoichiometric reactions of this type involving cyclic π -hydrocarbons have been nucleophilic additions (Nu = hydride, amines, phosphites, phosphanes, alkoxides, carbanions etc.) to the $[(\eta^5\text{-cyclohexadienyl})Fe(CO)_3]^+$ cation **115** [146] as well as carbanion attack on the arene ring of $(\eta^6\text{-arene})Cr(CO)_3$ complexes **116** [147] (Fig. 46).

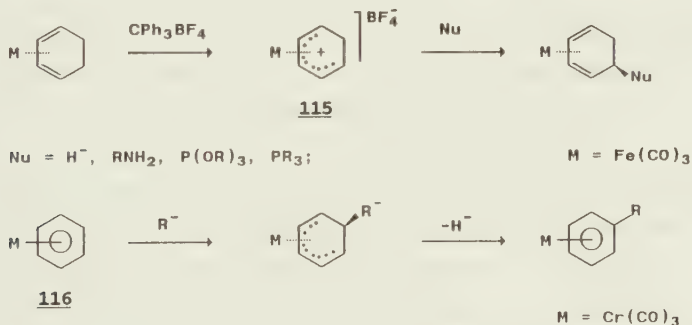


Figure 46

With the parent compound **115**, these reactions always proceed highly regio- and stereoselectively, occurring at the dienyl terminus and at the face of the complex anti to the metal. With unsymmetrically monosubstituted complexes the regioselectivity depends on the substituents. A wide range of novel routes has

been developed to synthesize organic molecules often inaccessible by conventional strategies [148,149]. The development of general rules for the regioselectivity of nucleophilic attack on cationic π -hydrocarbons has made these reactions more predictable and thereby further enhanced their potential [150].

Stable $[(\text{dienyl})\text{Fe}(\text{CO})_3]^+$ cations are readily available from the corresponding $(\text{diene})\text{Fe}(\text{CO})_3$ complex by hydride abstraction, protonation of uncomplexed double bonds or protonation of ethers, alcohols or acetates.

Tertiary phosphanes [151] and phosphites have proven to be particularly convenient nucleophiles as they undergo clean addition to the dienyl ligand to yield stable phosphonium salts and phosphonate adducts. $[(\eta^5\text{-cyclohexa-2,4-dienyl})\text{Fe}(\text{CO})_3]^+\text{BF}_4^-$ **115** (Fig. 47) reacts with a number of nucleophiles to give stable $(\text{cyclohexadiene})\text{Fe}(\text{CO})_3$ derivatives. Birch and co-workers [152] have reported that phosphites add to form the phosphonium salt and suggested that a facile solvent catalyzed Michaelis-Arbusov reaction yields the phosphonate diester. Hafner et al. [153] have re-investigated this reaction using $[(\text{cycloheptadienyl})\text{Fe}(\text{CO})_3]^+\text{BF}_4^-$ **117** and isolated $(5\text{-(dimethylphosphonato)-cyclohepta-1,3-diene})\text{Fe}(\text{CO})_3$ and a stoichiometric amount of $[\text{CH}_3\text{P}(\text{OCH}_3)_3]^+\text{BF}_4^-$. The formation of this by-product suggests that the initially formed trialkoxyphosphonium salt is dealkylated in an Arbuzov-type reaction and that the reaction proceeds by an autocatalytic mechanism. The same authors have extended these reactions to acyclic dienyl derivatives which are easily converted into their corresponding phosphonium salts and phosphonates. Triphenylphosphane addition to the $[(\eta^5\text{-2,4-hexadienyl})\text{Fe}(\text{CO})_3]^+\text{BF}_4^-$ complex proceeds anti to the tricar-

bonyliron group at the sterically less hindered end to yield the cisoid diphenylphosphonium salt. On the other hand, addition of trialkyl phosphite to the same complex produces two regioisomeric phosphonium salts which can be transformed to their corresponding phosphonates in a base-catalyzed reaction and used in Wittig-Horner reactions.

The low-temperature addition of tertiary phosphites to allylic cations (e.g. $[(\text{allyl})\text{Fe}(\text{CO})_4]^+\text{X}^-$) proceeds regio- and stereoselectively to give coordinated β -olefinic trialkoxy phosphonium salts, which on reaction with an excess of triethyl phosphite yields the uncomplexed (2-alken-1-yl)-triethoxy-phosphonium salts. These can be converted to their corresponding phosphonates in 90% yield on treatment with sodium bicarbonate [153].

5.2 Nucleophilic Addition of Lithium Dialkyl Phosphites to Metal-Coordinated Cyclic Carbenium Ions

We have developed a very fast and novel method for the synthesis of metal-coordinated cyclic phosphonates. Dialkyl phosphites are known to be deprotonated by lithium-*t*-butylate and potassium-*t*-butylate in methylene chloride or tetrahydrofuran at -60°C and undergo highly diastereoselective additions to N-glycosyl-nitrones [154].

Deprotonation of dialkyl phosphites in tetrahydrofuran or ether at -78°C by *n*-butyl- or phenyllithium yields the corresponding lithium dialkyl phosphite anions, which on addition of $[(\text{cyclohexadienyl})\text{Fe}(\text{CO})_3]^+\text{BF}_4^-$ **115** at -50°C cleanly form their corresponding (cyclohexadiene) $\text{Fe}(\text{CO})_3$ phosphonate diesters **118-120** (Fig. 47).

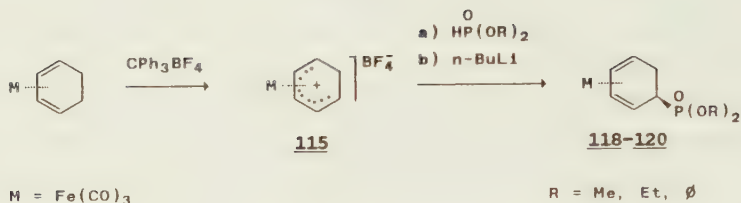


Figure 47

The phosphites employed were dimethyl phosphite, diethyl phosphite and diphenyl phosphite. The removal of the solvent and subsequent flash-chromatography gave the products in yields of 80-90%. The reaction time is about 15 minutes which is much faster than the procedures described by Birch [152] and Hafner [153]. The stereochemistry of the reaction has not been investigated, but the configuration shown is assumed to result from attack opposite to the $\text{Fe}(\text{CO})_3$ group, analogous to all other reactions of this type so far examined [146].

To determine the scope of this reaction the [(cycloheptadienyl)- $\text{Fe}(\text{CO})_3$] $^+\text{BF}_4^-$ complex 117 was synthesized and the addition was carried out using the same procedure as described above (Fig. 48).

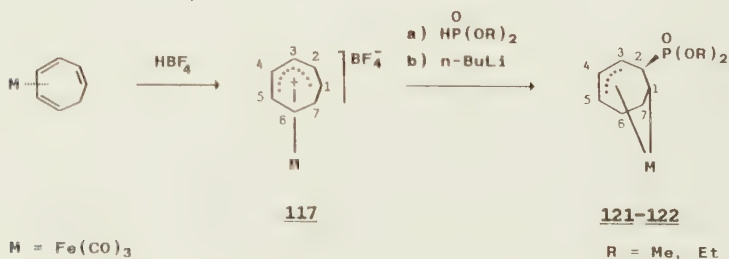
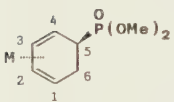
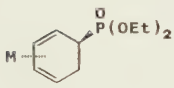
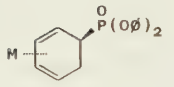
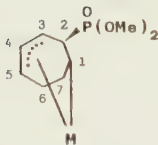
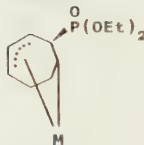


Figure 48

Hafner [153] had previously shown that the addition of trimethyl phosphite to the cycloheptadienyl complex gave 5-(dimethylphosphonato)cyclohepta-1,3-diene)Fe(CO)₃.

The ¹³C-NMR data obtained for the product from the lithium dimethyl phosphite addition does not correspond to the data found by Hafner [153]. The spectrum consists of the signals of five CH-groups, one of which shows a very large (P,C) coupling (124.0 Hz) and can be assigned to a carbon directly bonded to phosphorous. There are also two methylene groups in the spectrum, but only one of them (C(7)) shows a coupling to phosphorous (J(P,C)=7.2 Hz). The four remaining CH-groups have chemical shifts of 99.8, 80.8, 57.3 and 17.9 ppm and these shifts are in accord with values found for carbons bound to iron. Initially, a product of the expected type 118 (see Fig. 47) but of opposite stereochemistry at C(2) was assumed, formed by initial attack at the metal followed by migration to the hydrocarbon ring from the iron side. However, ¹³C-NMR data do not correspond to those of a typical (diene)Fe(CO)₃ ¹³C chemical shift pattern and therefore this structure was discarded. The resonance found at 17.9 ppm is of particular significance as it suggests that a carbon-iron σ-bond is present in the molecule. The three remaining chemical shifts form part of a η³-allyl system with the resonance at 99.8 ppm assigned to the central carbon atom C(4). The shifts at 80.8 and 57.3 ppm represent carbon atoms C(5) and C(3) (Fig. 48). ¹³C chemical shifts and J(P,C) of these compounds are summarized in Table 9.

^{13}C CHEMICAL SHIFTS OF SUBSTITUTED CYCLIC (DIENE) $\text{Fe}(\text{CO})_3$ COMPLEXES IN C_6D_6

Compound	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	R	∞
 118	60.2 (10.1)	85.8	85.0 (3.9)	56.0 (9.1)	34.1 (134.2)	25.5	-	53.0 (6.5)	211.0
 119	61.0 (9.7)	85.8	85.5 (4.1)	57.7 (8.9)	35.0 (134.1)	26.1	-	61.8 (6.6) 16.4 (4.9)	211.8
 120	59.6 (8.6)	85.9	85.5 (3.3)	54.8 (11.4)	34.9 (131.4)	25.5	-	129.6 128.8 125.4 120.8	210.7
 121	17.9 (11.6)	45.3 (124.0)	57.3	99.8 (4.1)	80.8	27.7	39.2 (7.2)	53.0 (7.6) 52.8 (7.4)	214.2
 122 M = $\text{Fe}(\text{CO})_3$	17.9 (11.6)	45.5 (124.4)	57.3	99.3 (4.1)	80.2	27.3	39.0 (7.1)	61.9 (7.5) 61.5 (7.3) 16.1 (2.3) 16.0 (2.7)	213.8

(δ ^{13}C in ppm relative to TMS; J(P,C) in parentheses (Hz))

The proposed structure 121 is in agreement with products obtained in other addition reactions of nucleophiles to cycloheptadienyl complexes. Thus, the reduction of (cycloheptadienyl)Fe(CO)₃⁺ 117 with sodium borohydride was originally reported to give only (cycloheptadiene)Fe(CO)₃ [155]. However, Aumann [156] has since shown that a mixture of products, namely the 1,3-diene complex and a σ,π -allyl complex, are formed as a result of attack at C(1) and C(2) of the cycloheptadienyl complex. The proportion of each compound depends on the reaction conditions and the nucleophile employed and can also vary with the nature of the other ligands in the compound. In cases where a carbon monoxide ligand is replaced by triphenylphosphane, nucleophilic attack generates solely σ,π -allyl products resulting from attack at C(2) of (cycloheptadienyl)Fe(CO)₃⁺ [157].

The addition of lithium diethyl phosphite to the cycloheptadienyl complex was also carried out and generates the σ,π -allyl phosphonate diethyl ester with practically unchanged ¹³C chemical shifts for the hydrocarbon system. Yields for both reactions are in the 85-90% range and reaction time is about 15 minutes.

The proton spectra of both σ,π -allyl complexes are also very similar. The three allylic protons can be found at 4.65, 4.15 and 3.97 ppm in the case of the dimethyl phosphonate and at 4.45 and in the range of 4.0-3.8 ppm for the diethyl phosphonate. The latter signals have the same chemical shift as the methylene protons of the phosphonate and are therefore not resolved. The proton bound to the carbon adjacent to phosphorous is a doublet of triplets with a chemical shift of 3.32 ppm and 3.34 ppm and shows a large J(P,H) coupling (21.9 Hz, 21.3 Hz), for 121 and

122, respectively. The proton H-C(2) also couples to H-C(3) ($J=6.7$ Hz, 6.5 Hz) and to H-C(1). The latter proton has a chemical shift of 1.30 ppm (dimethyl phosphonate) and 1.39 ppm (diethyl phosphonate) which is characteristic for protons adjacent to a carbon-iron σ -bond. All assignments were determined by selective decoupling experiments.

This novel reaction is a useful alternative to the addition of trialkyl phosphite to cationic cyclohexadienyl iron complexes as it proceeds in one step and in yields of 80-90%.

6. ⁵⁷Fe-NMR SPECTROSCOPY

6.1 Introduction

The investigation of transition metal NMR spectroscopy of organometallic compounds has long been hampered by a lack of sensitive detection methods. Recently, the development of stable superconducting high-field magnets for NMR spectrometers, together with broadband r.f. probes, programmable pulse generators and new pulse sequences has improved NMR detection of many insensitive low frequency transition metal nuclei. In consequence, the evaluation of structural information contained in NMR data, i.e. chemical shifts, heteronuclear and homonuclear coupling constants as well as relaxation times, has shown great potential for organometallic chemistry and homogeneous catalysis [158,159].

Experimental difficulties in the detection of transition metal resonances are most often caused by the low natural abundance and low sensitivity, i.e. low receptivity, and by the magnetic properties of the nuclei under investigation. Small magnetic moments lead to low Larmor frequencies and for spin- $\frac{1}{2}$ nuclei to long longitudinal and transversal relaxation times T_1 and T_2 . Nuclei with spin ≥ 1 often have large electric quadrupole moments which give rise to short T_1 and T_2 values, the latter being responsible for the large experimental line width (up to 30 KHz).

The nucleus ^{57}Fe as shown in Table 10 has a spin $I = \frac{1}{2}$, one of the smallest magnetic moments and a natural abundance of 2.2% leading to a receptivity of only 0.4% of that of the ^{13}C nucleus.

Table 10

NMR properties of some Group VIII transition metal nuclei

Nucleus	^{57}Fe	^{103}Rh	^{187}Os	^{195}Pt
Spin [$\hbar$]	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$
Frequency (MHz, 9.4T)	12.9	12.6	9.1	86.0
Magnetic Moment (nuclear magnetons)	0.0902	-0.0883	0.0643	0.61
% Isotope	2.2	100	1.6	33.7
Sensitivity $^{13}\text{C} = 1.0$	0.002	0.002	0.001	0.63
Receptivity	0.004	0.18	0.002	21.1
Chemical Shift Range (ppm)	12000	10000		13000

6.2 Methods

In FT-NMR spectroscopy the NMR-Signal is measured by the summation of many single free induction decays (FIDs). Experimental parameters for the detection of transition metal nuclei may be optimized if the relaxation times are known [160]. Long relaxation times necessitate long delays between two successive r.f. pulses in order to avoid intensity anomalies as well as achieving an optimum signal/noise ratio for a given pulse angle.

High magnetic fields increase the sensitivity not only because of the correlation with B_0 but also because of the much more effective T_1 -relaxation. Experiments using polarization transfer techniques, such as INEPT [161] and DEPT [162], may be applied if a scalar coupling of the metal to a ligand atom such as hydrogen, phosphorus or fluorine exists [163]. Special probeheads are, however, necessary if the polarization is not transferred from a proton as pulsing has to occur on two channels with different frequencies. It is advantageous if a large coupling can be used for the polarization transfer. A prerequisite for the successful application of these pulse techniques is the optimization of the parameters of the INEPT and DEPT experiments [164]. The maximum enhancement factor to be expected for polarization transfer from nuclei A to nuclei X is given by the ratio $\gamma(A)/\gamma(X)$. This ratio varies from 30 for (^1H)- ^{57}Fe to about 13 for (^{31}P)- ^{57}Fe . The pulse sequence repetition rate in these double-resonance experiments depends only on T_1 of the donor and thereby an additional gain in sensitivity is achieved. In heterodiene and diolefin iron complexes no such couplings of the metal to the ligand have been resolved. An efficient approach for the measurement of low γ transition metal nuclei is based on indirect 2D spectra via the observation of

sensitive nuclei such as ^1H or ^{31}P [165]. This method is again limited to compounds in which a scalar coupling to the metal nucleus is observed. In addition to the chemical shift the couplings to the X nucleus can be determined.

The disadvantages of long relaxation times can also be avoided by applying the steady state technique [166]. This method in contrast to the INEPT pulse sequence is also useful when large frequency ranges have to be screened. Additionally the steady-state technique can also be used for the determination of T_1 and T_2 . For nuclei with long relaxation times, such as ^{57}Fe , the decay of the FID is not determined by T_2 , but by the inhomogeneity of the static field ($1/T_2^* = 1/T_2 + \gamma\Delta B_0/2$). After each r.f. pulse, the NMR signal is detected only during a time comparable with T_2^* , whereas the waiting time between successive r.f. pulses is comparable with T_1 . This means that the NMR signal is obtained only during a very small part of the total measuring time.

In the steady state method equal and coherent r.f. pulses are applied periodically to the sample. After a build-up time a steady state is established in the spin system, i.e. the magnetization vector shows exactly the same position during any pulse period. The Boltzmann equilibrium population of the spin system or the magnetization M_0 in the direction of the static magnetic field B_0 is never reached. The magnetization vector always has a longitudinal and a transverse component and therefore at any time a combination of longitudinal and transverse relaxation takes place. The steady state magnetization depends in a complicated manner on the experimental parameters such as pulse period, flip angle, the difference between Larmor frequency and carrier frequency of the r.f. pulse, and also on the ratio T_1/T_2 [166]. The gain in

sensitivity achieved for the same experimental time is directly proportional to the square root of the T_2/T_2^* ratio :

$$S/N \text{ (steady state)} = S/N_{(\text{conv})} \cdot (T_2/T_2^*)^{\frac{1}{2}}$$

6.3 Chemical Shifts

The magnetic field experienced by the nucleus is never equal to the applied field, but depends on the magnetic environment in which the nucleus is found. The perturbation of the field is caused by the electrons in the vicinity of the nucleus which produces a secondary field at the nucleus. This is reflected in the reduced Larmor frequency ν by the introduction of a screening constant σ :

$$\nu = \gamma B_0(1-\sigma)/2\pi$$

There are two contributions to σ , the diamagnetic term σ_d and the paramagnetic term σ_p , which are opposite in sign :

$$\sigma = \sigma_d + \sigma_p$$

The magnitude of σ_d is largely determined by the s-electron density at the nucleus and is of dominant importance for the proton resonance. The variation of the negative paramagnetic contribution σ_p is substantial for atoms with many electrons in the outer orbitals involved in chemical bonding. Several factors determine its magnitude :

- a) The inverse of the energy separations ΔE between the ground and excited electronic states of the molecule.

- b) The bond order term ΔQ which describes the relative electron densities in the various p-orbitals involved in bonding. For metals or heavier atoms p-orbitals are ignored and d-orbitals are considered.
- c) The average inverse cube distance $\langle 1/r^3 \rangle$ from the nucleus to the orbitals concerned.

These factors can be summarized in the following equation :

$$\sigma_p \propto (\Delta E)^{-1} \cdot \langle 1/r^3 \rangle \cdot \Delta Q$$

More distant electrons give rise to long range effects on σ_d and σ_p which are quite large but very often cancel out and are usually neglected. It is believed that for transition metal nuclei where even small structural changes cause large variations in chemical shifts the variation of the paramagnetic term is dominant [167].

Iron chemical shifts are expressed relative to neat Fe(CO)_5 as an external reference. This resonance frequency at the low frequency end of the scale is well known as a function of temperature and solvent [168]. The range of ^{57}Fe chemical shifts in diamagnetic compounds covers approximately 12000 ppm which at a field of 9.4 T corresponds to 150 KHz. In general, the formal oxidation state of iron in organometallic and inorganic complexes determines the chemical shift position on the shift scale. Resonance frequencies of Fe(II) -complexes are found at high frequencies while those of Fe(0) compounds are found at low frequencies. Intermediate chemical shifts have been determined for ferrocenes [169-173] and cationic olefin compounds [174]. The chemical shift of structurally very similar complexes with

different charges is strongly influenced by the charge density at the nucleus. In the series of η^3 -allyl- $(\text{Fe}(\text{CO})_3)\text{X}$ - [175] and $\text{Cp}(\text{Fe}(\text{CO})_2)\text{X}$ -complexes [176] the deshielding of the ^{57}Fe resonances semi-quantitatively correlates with electronegativity values of the substituents. Substitution by an electron withdrawing group at the ligand causes high frequency shifts of up to 500 ppm. An interesting stereoelectronic phenomenon is the subtle dependence of the chemical shift (δ ^{57}Fe) on the position as well as on the steric effects of the alkyl substituents. Within a group of cyclic (η^4 -diene) $\text{Fe}(\text{CO})_3$ complexes shielding decreases with increasing ring size. Strongest deshielding can be observed for those alkyl substituted (butadiene) $\text{Fe}(\text{CO})_3$ complexes in which the terminal carbon atom is most strongly rehybridized [175]. Similar deshielding effects have also been observed in some alkyl substituted $[(\text{allyl})\text{Fe}(\text{CO})_4]\text{X}$ -complexes. Furthermore, a correlation between thermal stability and shielding of the iron resonance has been found within both series of complexes [175].

In addition, electronegative heteroatoms directly bound to the metal, e.g. in the iron(II) porphyrin complexes and in (heterodiene) $\text{Fe}(\text{CO})_3$ complexes, cause additional large deshielding effects.

The chemical shifts of the heme protein carbonmonoxymyoglobin [177,178] and two other iron porphyrin complexes [173,179] are all found in the 7000-9500 ppm range. The short spin-lattice relaxation times found for these very large complexes considerably simplifies the detection of the ^{57}Fe -resonance.

6.4 Coupling Constants

Information on scalar coupling constants in literature is relatively scarce. One-bond (^{57}Fe , ^{13}C) and (^{57}Fe , ^{31}P) coupling constants have been observed from the satellite systems of ^{13}C and ^{31}P NMR spectra of various ferrocene [169,180] and carbonyl complexes [181]. Very little variations have been found in both groups with values ranging from 4-5 Hz in the case of ferrocene to 22-31 Hz for iron carbonyl complexes [10]. In phosphine complexes of type $\text{Fe}(\text{CO})(\text{NO})_2\text{L}$ (^{57}Fe , ^{31}P) couplings range from 47.2-62.4 Hz and show a tendency to decrease as the electronegativity of the phosphine decreases [167]. Direct determinations of $J(^{57}\text{Fe}, ^{31}\text{P})$ in diphosphaferrocenes [158] and by a (^{31}P)-Fe INEPT experiment for $\text{Fe}(\text{CO})_2(\text{PMe})_2\text{CS}_2$ have been reported ($J=31$ Hz) [163]. $J(^{57}\text{Fe}, ^1\text{H})$ and $J(^{57}\text{Fe}, ^{31}\text{P})$ couplings were determined from reverse 2D $^1\text{H}\{-^{57}\text{Fe}\}$ and $^{31}\text{P}\{-^{57}\text{Fe}\}$ experiments [165] of $(\eta^5\text{-cyclopentadienyl})(1,2\text{-ethanediyl-bis(diphenylphosphane)})\text{FeH}$ ($J(\text{Fe}, \text{H}) = 9.3$ Hz, $J(\text{P}, \text{Fe}) = 61.6\text{Hz}$), $(\eta^4\text{-butadiene})_2\text{FePMe}_3$ ($J(\text{Fe}, \text{P}) = 61.3$ Hz) and $(\eta^4\text{-butadiene})_2\text{FePEt}_3$ ($J(\text{Fe}, \text{P}) = 62.0$ Hz). These values are significantly larger than those found in $\text{Fe}(\text{CO})_4(\text{PEt}_3)$ and suggest that there is more σ -character in the Fe-P bond for these three complexes.

^{15}N NMR study of iron (II) low spin complexes of ^{15}N and ^{57}Fe labelled porphyrin has determined the only (^{57}Fe , ^{15}N) coupling to date ($J(\text{Fe}, \text{N}) = 7.8$ Hz) [182].

6.5 Relaxation

If a physical system is perturbed from its equilibrium position and then the perturbing influence is removed the system will take a finite time to readjust to the original conditions. The system is said to relax.

The knowledge of relaxation times of insensitive spin $\frac{1}{2}$ nuclei, such as ^{57}Fe , is of great importance in the choice of parameters for the detection of such resonances. Two mechanisms contribute to the longitudinal relaxation rate of ^{57}Fe (T_1). These are the field independent contribution due to Spin-Rotation (SR) and a quadratically field dependent one due to Chemical-Shift-Anisotropy (CSA).

The motion of the molecular magnetic moment arising from the electronic distribution within the molecule produces fluctuating magnetic fields which cause relaxation. This mechanism is called the Spin-Rotation mechanism and is found to dominate in small, isotropic molecules such as $\text{Fe}(\text{CO})_5$. Contrary to dipole-dipole and CSA relaxation rate the SR relaxation rate is directly proportional to temperature.

The magnetic screening of the metal nuclei by the surrounding electron is dependent on the orientation of the molecular axis relative to the applied magnetic field B_0 . Molecules in liquids undergo Brownian motion, i.e. they are diffusing and rotating randomly so that the nuclear magnets in the system are continually moving relative to each other and thus produce fluctuating fields at all points within the sample. Over the long term these average out to zero, but at any instant the sample will contain a component of random phase and intensity at the nuclear resonant frequency and it is this which effects

interchange of nuclear energy and thereby allows the system to relax. The contribution of the CSA mechanism to $1/T_1$ is proportional to the square of the applied field B_0 and if CSA is the only mechanism operating then $7/6 T_1 = T_2$. Dipole-dipole relaxation is caused by the magnetic fields of nearby nuclear dipoles. The magnitude of this interaction depends on the square of the magnetogyric ratios and on the sixth power of the distance between the interacting nuclei. To determine the relative contributions of the two mechanism SR and CSA to the longitudinal relaxation T_1 it is necessary to measure their field or temperature dependence.

When using high-field superconducting magnets it is possible to determine ^{57}Fe relaxation times T_1 by the inversion recovery technique [183,184]. At low fields CSA does not dominate all other relaxation mechanisms and, therefore, T_1 is relatively long and, the steady state technique is applied to avoid long waiting times.

In addition to the longitudinal relaxation T_1 the transverse relaxation time T_2 causes spins to lose their coherence when the external field B_1 (pulse) is switched off and the spins spiral back to their equilibrium position. The transverse magnetization T_2 is also influenced by small amounts of particles or by any paramagnetic impurities in the samples. The preparation of degassed samples is therefore essential as oxygen in its triplet state acts as a paramagnetic relaxation reagent.

Spin-lattice relaxation times of the ^{57}Fe nucleus have been reported for neat liquid $\text{Fe}(\text{CO})_5$ $T_1 = 80 \pm 10$ s (293K) and for ferrocene (1M in C_6D_6) $T_1 = 4 \pm 1$ s (303K; $B_0 = 7.05\text{T}$) [184]. T_1 for tert-butylferrocene has been determined in different magnetic fields. Values range from 4 s at 4.2T to 0.6 s at 11.7T

[173]. Very short relaxation times have been measured for carbonmonooxymyoglobin in a field $B_0 = 8.5$ T $T_1 = 17 \pm 3$ ms [178] and in a field $B_0 = 11.7$ T $T_1 = 30$ ms [177].

Contradictory explanations for T_1 mechanisms are found in literature for ferrocene [179] and tert-butylferrocene [173]. In a thorough investigation of the contributions of different relaxation mechanisms to T_1 , the relaxation times of various iron complexes [$\text{Fe}(\text{CO})_5$, ferrocene, (butadiene) $\text{Fe}(\text{CO})_3$, (isoprene) $\text{Fe}(\text{CO})_3$, (Z)- and (E)-(pentadiene) $\text{Fe}(\text{CO})_3$] were determined at two different fields B_0 , 2.1 T and 9.4 T at temperatures ranging from 275 K to 321 K. The SR mechanism is found to be the only spin lattice mechanism for $\text{Fe}(\text{CO})_5$, whereas for the other compounds under investigation CSA is the principal process at higher magnetic fields while SR dominates at 2.1 T. At $B_0 = 9.4$ T, typical T_1 values of (diene) $\text{Fe}(\text{CO})_3$ complexes range from 19–28 s [186].

6.6 New Results and Discussion

The interpretation of ^{57}Fe chemical shifts has hitherto been limited to largely qualitative analysis. It has been shown that the relative ^{57}Fe chemical shifts correlate well with expected charge densities at the iron nucleus. However, the discussion of changes in charge densities are only applicable in the interpretation of chemical shifts within a given class of compounds or when studying ligand exchange at the metal. Slight modification to the structure of a ligand, e.g. introduction of a methyl substituent, causes appreciable changes in the chemical shift, but these are more difficult to interpret. A systematic study of a well-defined class of compounds is therefore necessary to determine these effects.

Electronegative heteroatoms bound directly to the metal cause large deshielding effects. This has also been observed for other transition metals, e.g. cobalt, rhodium [187].

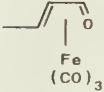
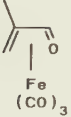
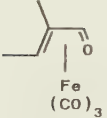
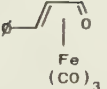
A number of (enone)Fe(CO)₃ complexes have been particularly useful in the synthesis of (η^4 -diene)Fe(CO)₃ complexes when the complexing dienes are sensitive to thermolysis or photolysis. The (enone)Fe(CO)₃ complex **14** acts as a transfer agent for the Fe(CO)₃ unit [43]. The fact that enone complexes are thermally unstable is reflected in their very high ⁵⁷Fe chemical shifts relative to Fe(CO)₅ which are found in the region of ferrocene. This confirms the finding that transition metal chemical shifts are a measure of transition metal complex stability [159].

In one part of this work a series of methyl and phenyl substituted (enone)Fe(CO)₃ complexes **123-132** and **14** were synthesized and their ⁵⁷Fe chemical shifts were determined. The results of this investigation are summarized in Table 11. The results have been divided into two groups, complexes of aldehydes and complexes of ketones. These show markedly different behaviour as far as methyl substitution is concerned. The chemical shift of (propenal)Fe(CO)₃ **123** is 50 ppm lower than that of (3-buten-2-one)Fe(CO)₃ **128**. This difference is also reflected in the shifts of substituted aldehydes and ketones.

The effect of methyl substitution is much less apparent in aldehydes than in ketones. Methyl substitution in position 4 causes shift of 10 ppm in ketone complexes and about 5 ppm in aldehyde complexes. In ketone complexes a methyl group on C(3)

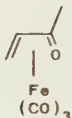
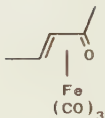
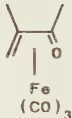
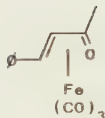
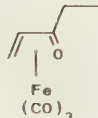
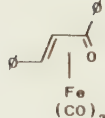
TABLE 11

⁵⁷Fe CHEMICAL SHIFTS OF (HETERODIENE)Fe(CO)₃ COMPLEXES IN C₆D₆, T = 296K

Nr.	Compound	⁵⁷ Fe ^{a)} [ppm]
<u>123</u>		1274
<u>124</u>		1279
<u>125</u>		1279
<u>126</u>		1277
<u>127</u>		1504

a) Chemical shifts $\delta^{57}\text{Fe}$ are reported relative to (butadiene)Fe(CO)₃ with an error of ± 1 ppm.

TABLE 11 (continued)

Nr.	Compound	$\delta^{57}\text{Fe}$ ^{a)} [ppm]
<u>128</u>		1325
<u>129</u>		1335
<u>130</u>		1349
<u>14</u>		1560
<u>131</u>		1318
<u>132</u>		1688

a) Chemical shifts $\delta^{57}\text{Fe}$ are reported relative to (butadiene) $\text{Fe}(\text{CO})_3$ with an error of ± 1 ppm.

deshields by about 25 ppm but only by 5 ppm in aldehyde complexes for the respective carbon. The introduction of a phenyl substituent at the terminal olefinic carbon deshields in both types of complexes by 230-235 ppm. In ketone complexes the substitution of the methyl group at C(2) by a phenyl group deshields by an additional 120 ppm, while an ethyl group instead of a methyl group in position 2 shields by 7 ppm.

In addition to the (heterodiene)Fe(CO)₃ complexes the chemical shift of two other iron complexes were determined. The synthetic utility of Davies' acetyl complex **56** has been described earlier (see Chapter 2.8). The synthesis of this complex was accomplished by published methods [88].

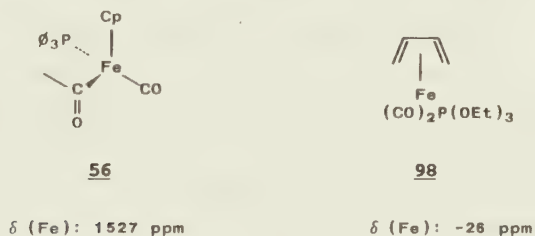


Figure 49

The ⁵⁷Fe chemical shift of this compound (C₆D₆, 296±1K) was found to be 1527 ppm which is in the same range as those shifts found for ferrocene (1535 ppm) and phenyl substituted enone complex **14** (1560 ppm) (Fig. 49). The triphenylphosphane and the carbon monoxide ligand are both η²-ligands while the acetyl group is σ-bonded. The combination of these three ligands cause the same low-field shift as a second cyclopentadienyl ligand (ferrocene). The chemical shift (δ ⁵⁷Fe) and the (⁵⁷Fe, ³¹P) coupling were determined in a conventional one-pulse experiment. The value of J(Fe,P) = 59 Hz is comparable to those found by Benn and

Brevard [165] for their phosphine complexes. It is quite a lot larger than (Fe,P) couplings in $\text{Fe}(\text{CO})_4\text{L}$ complexes [181]. In the course of our ligand exchange reactions the synthesis of (butadiene) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ **98** gave the opportunity to determine the electronic effects of a substitution of phosphite for carbon monoxide on the metal nucleus. The high-field shift of -26 ± 1 ppm relative to (butadiene) $\text{Fe}(\text{CO})_3$ suggests that tertiary phosphites are better electron donors than carbon monoxide thereby increasing the electron density at the iron. An even larger coupling constant has been determined for this phosphite complex ($J(\text{Fe},\text{P})=88$ Hz).

6.7 Determination and Discussion of Longitudinal Relaxation Time

The conventional inversion-recovery technique was used for the determination of T_1 at 12.97 MHz. Long measuring times are compensated by the fact that experimental errors in setting 90° and 180° pulse angles have only small effects on the overall result. The pulse sequence for this experiment can be described as follows :

The initial state of the spins is established by a non-selective 180° pulse. After a time τ , a non-selective 90° pulse is applied and the entire free induction decay following is recorded. After a delay time D, which has to be five times larger than the expected T_1 to permit magnetic equilibration, the experiment is repeated n times. By variation of τ one is able to determine the intensity of each signal as a function of τ . For a faster determination of the infinite magnetization $I(\infty)$ only the last $\pi/2$ pulse of the above pulse sequence is used. The intensity $I(\tau)$ of a signal can be described by

$$I(\tau) = I(\infty) (1 - 2e^{(-\tau/T_1)})$$

Changes in sensitivity and resolution due to inhomogeneity of the magnetic fields in accumulation of data over long periods of time have to be minimized. This is accomplished by saving FIDs belonging to the same delay. After n experiments with τ_1 the FIDs are saved in a block and then n experiments with the next delays $\tau_2 \dots \tau_i$ are completed and saved. This sequence is repeated x times, thereby distributing the same outside influences to all experiments.

The relaxation time T_1 for ((E)-4-phenyl-3-buten-2-one) $\text{Fe}(\text{CO})_3$ **14** was determined in a series of six experiments ($\tau = 0.1, 0.5, 1, 4, 10, \text{ and } 40 \text{ s}$) and found to be 4 s . This is a much shorter relaxation time than the value determined for (diene) $\text{Fe}(\text{CO})_3$ complexes which range from $19\text{--}28 \text{ s}$ [175]. The CSA mechanism is probably also dominant at this field. The shielding at a given nucleus varies with the molecular orientation in the static field B_0 . Molecular tumbling therefore modulates the local magnetic field and influences relaxation. The large phenyl substituent of **14** could slow down molecular tumbling thereby increasing the correlation time τ_c . This increase in τ_c according to the following equation :

$$T_1^{-1} = 2/15 \gamma_A^2 B_0^2 \Delta\sigma^2 \tau_c$$

causes an increase in the relaxation rate T_1^{-1} and therefore a decrease in T_1 . Furthermore, the mechanism for CSA is influenced by the shielding anisotropy $\Delta\sigma$. If the molecular axis of a molecule is oriented parallel or perpendicular to B_0 then differing shielding constants $\sigma_{\parallel}$ and $\sigma_{\perp}$ will act. A large $\Delta\sigma$ will increase the rate of relaxation and shorten T_1 . The large phenyl group could influence the shielding anisotropy in this way.

7. EXPERIMENTAL PART

Proton NMR spectra were recorded on a Varian XL-200 spectrometer at 200 MHz or a Bruker AM-400 spectrometer at 400 MHz in 5mm sample tubes. The ^{13}C -NMR spectra were recorded at 25.2 MHz on a Varian XL-100, at 50.4 MHz on a Varian XL-200 or at 100.8 MHz on a Bruker AM-400 spectrometer in 10 mm sample tubes. The chemical shifts $\delta(\text{ppm})$ are reported relative to tetramethylsilane (TMS) as the internal standard. Multiplicities s (singlet), d (doublet), t (triplet), q (quartet), qt (quintett), m (multiplet), coupling constants in Hertz (Hz), relative intensities and assignments are given in parentheses.

The ^{31}P -NMR spectra were recorded at 80.7 MHz on a Varian XL-200 spectrometer. Chemical shifts $\delta(\text{ppm})$ are reported relative to H_3PO_4 as the external reference (uncorrected).

The ^{57}Fe -NMR spectra were measured at 12.97 MHz (9.4 T) on a Bruker AM-400 spectrometer. The spectra were recorded using rotating sample tubes (diameter 20 mm, volume height 40-45 mm) at a temperature of 296 ± 1 K. A pulse angle of 60° ($70 \mu\text{s}$) and recycle delay of 5 s were used and between 5000-10000 transients were completed. To improve the signal/noise ratio the FID was treated by a Lorentz function ("sensitivity enhancement"). Chemical shifts $\delta(\text{ppm})$ are reported relative to (butadiene)- $\text{Fe}(\text{CO})_3$ and as the external reference.

Solutions in C_6D_6 of (heterodiene) $\text{Fe}(\text{CO})_3$ complexes were prepared under an inert gas atmosphere and filtered through aluminum oxide (Merck 90 activation II-III) directly into the sample tubes. For the T_1 measurement the sample was degassed

with three freeze-pump-thaw-cycles and the tube sealed under vacuum. For further details see p. 84f and [175, 186].

Infrared spectra (IR) were recorded on a Perkin-Elmer 298 spectrometer. The wave numbers in cm^{-1} are characterized by s (strong), m (medium), w (weak), sh (shoulder), and br (broad). Assignments are given in parentheses.

Mass spectra (MS) were recorded on a Varian-MAT-711 spectrometer at 70 eV.

Melting points (m.p.) were determined on a Buchi 510 apparatus and are uncorrected.

Thin layer chromatography (TLC) was carried out on a 0.25 mm precoated silica gel aluminium plates (Merck, Kieselgel 60 F₂₅₄) or on 0.20 mm precoated silica gel plastic sheets (Macherey-Nagel, Polygram SIL N-HR/UV₂₅₄).

Column chromatography was performed on silica gel (Merck, Kieselgel 60) mesh 70-230 for normal chromatography, 230-400 mesh for flash chromatography and for low-pressure chromatography (0.2-1.2 atm) Merck Li-Chroprep Si 60 was used.

Common solvents were distilled prior to use, tetrahydrofuran (THF) and ether (Et₂O) with sodium/benzophenone and hexane over LiAlH₄ in an apparatus with continuous distillation. Benzene (Merck, p.a.) was refluxed with sodium and distilled.

7.1 Synthetic Part

7.2 (η^4 -Diene) $\text{Fe}(\text{CO})_3$ Complexes

Method a:

50mmol of the diene ligand and 55mmol $\text{Fe}(\text{CO})_5$ were dissolved in 400ml of absolute benzene and irradiated overnight at 40°C with a high pressure mercury lamp (Philips HPK, 125W). The solvent was removed under reduced pressure and the residue was filtered on an aluminum oxide column to remove $\text{Fe}(\text{CO})_4$ (green band eluted with hexane) and any (η^2 -diene) $\text{Fe}(\text{CO})_4$ complexes. Chromatography on silica gel yielded the pure compounds which could be isolated in yields of 60-80%.

Method b:

10mmol of the functionalized diene and 15mmol $\text{Fe}_2(\text{CO})_9$ were dissolved in 20ml of absolute benzene or ether stirred first at room temperature for $\frac{1}{2}$ h and then refluxed for 1-3h. The reaction was monitored by TLC. If after overnight reaction starting material was still present another equivalent of $\text{Fe}_2(\text{CO})_9$ was added. On completion the mixture was filtered through Celite, a short aluminum oxide column and concentrated on the rotary evaporator. The residue was chromatographed on silica gel and yields range from 55-80%.

7.3 (η^4 -Heterodiene) $\text{Fe}(\text{CO})_3$ Complexes

50mmol of the heterodiene ligand and 55-60mmol of $\text{Fe}(\text{CO})_5$ were irradiated overnight at 40-45°C with a high pressure mercury lamp (Philips HPK, 125W). The reaction was monitored by TLC and two products could be detected : the (η^2 -heterodiene) $\text{Fe}(\text{CO})_4$ and the (η^4 -heterodiene) $\text{Fe}(\text{CO})_3$ complex. The benzene solution was

filtered through Celite to remove any decomposed material and then refluxed to convert the ene-complex into the enone complex. Removal of the solvent and chromatography on silica gel yielded the pure compounds in 60-80% yield. The following compounds have already been described in the literature :

(propenal)Fe(CO)₃ 123 [188], ((E)-3-phenyl-propenal)Fe(CO)₃ 127 [41], (3-buten-2-one)Fe(CO)₃ 128 [189], ((E)-3-penten-2-one)Fe(CO)₃ 129 [45], ((E)-4-phenyl-3-buten-2-one)Fe(CO)₃ 14 and (1,3-diphenyl-2-propenone)Fe(CO)₃ 132 [43].

7.4 (5-8-η-β-Ionone)Fe(CO)₃ (57)¹

Complexation of β-ionone accomplished using Fe₂(CO)₉ - Method b. Yield 74% of 57; orange crystals m.p. = 56°C.

¹³C-NMR (50.4 MHz, CDCl₃) : 204.4 (s, C(9)); 117.1 (s, C(6)); 81.4 (d, C(7)); 70.3 (s, C(5)); 51.6 (d, C(8)); 42.3 (t, C(2)); 38.7 (t, C(4)); 35.2 (s, C(1)); 34.0 (q, C(12)); 29.8 (q, C(11)); 29.6 (q, C(10)); 24.0 (q, C(13)).

¹H-NMR (200 MHz, CDCl₃) : 5.65 (d, J=8.5, H-C(7)); 2.41 (d, J=8.5, H-C(8)); 2.17 (s, 3H, H-C(11)); 1.93 (m, 2H, H-C(4)); 1.59 (m, 4H, H-C(2), H-C(3)); 1.45, 1.40 (2s, 6H, H-C(10), H-C(13)); 1.21 (s, 3H, H-C(12)).

MS : 304 (M⁺-CO); 276 (M⁺-2CO); 248 (M⁺-3CO).

Microanalysis : calc. C : 57.80% H : 6.02%
found C : 57.62% H : 6.12%

1. Numbering of carbon skeleton in spectral data according to carotenoid convention

7.5 (5-8- η - β -Ionol)Fe(CO)₃ (**58a**), (**58b**)

To a well stirred solution of 2.05g (5.8mmol) (5-8- η - β -ionone)-Fe(CO)₃ (**57**) in 50ml of methanol/water 0.54g (14mmol) NaBH₄ were added in small portions. The reaction was monitored with TLC (ether/hexane 2/1) and on completion the solvents were evaporated under reduced pressure and the residue treated with water. Extraction with 3 x 50ml CH₂Cl₂, subsequent drying with Na₂SO₄ and column chromatography on silica gel gave 1.78g (5.33mmol) (92%) (5-8- η - β -ionol)Fe(CO)₃ (**58a**).

¹³C-NMR (25.2 MHz, CDCl₃) : 211.9 (s, CO); 113.8 (s, C(6)); 80.7 (d, C(7)); 71.3 (d, C(8)); 68.7 (s, C(5)); 67.5 (d, C(9)); 42.5 (t, C(2)); 38.9 (t, C(4)); 34.8 (s, C(1)); 34.2 (q, C(12)); 29.8 (q, C(11)); 25.9 (q, C(13)); 23.3 (q, C(10)); 19.5 (t, C(3)).

MS : 334 (M⁺); 306 (M⁺-CO); 278 (M⁺-2CO); 250 (M⁺-3CO).

Complexation of β -ionol using Fe₂(CO)₉ (Method b) gave two products separable by column chromatography (ether/hexane 2/1).

¹³C spectroscopic data of the first eluted compound (R_f=0.5) was identical with that found for the product **58a** obtained from the NaBH₄ reduction of (5-8- η - β -ionone)Fe(CO)₃ (**57**) (see above).

Compound **58b** has the following ¹³C spectroscopic data :

¹³C-NMR (25.2 MHz, CDCl₃) : 211.9 (s, CO); 114.8 (s, C(6)); 82.7 (d, C(7)); 72.9 (d, C(8)); 69.2 (s, C(5)); 63.6 (d, C(9)); 42.5 (t, C(2)); 38.9 (t, C(4)); 34.8, (s, C(1)); 34.2 (q, C(12)); 29.4 (q, C(11)); 24.9 (q, C(13)); 23.6 (q, C(10)); 19.5 (t, C(3)).

7.6 (2-5- η -5-(2',6',6'-Trimethyl-1'-cyclohexenyl)-3-methyl-2,4-pentadiene-1-nitrile)Fe(CO)₃ (60)
[(7-10- η - β -ionylideneacetonitrile)Fe(CO)₃]

Under a nitrogen atmosphere 1ml (20mmol) acetonitrile were added to 20ml dry THF and cooled to -78°C. Slow addition of 11ml (18mmol) n-BuLi (1.6M in hexane) generated the lithium salt which precipitates. Subsequently, 3.0g (9mmol) (5-8- η - β -ionone)Fe(CO)₃ (57) in 10ml of THF were added and a dark red solution was formed. The mixture was stirred at -78°C for 4h and then allowed to warm to RT overnight. Neutralisation with 10% HCl was followed by extraction with CH₂Cl₂. The organic phases were dried with Na₂SO₄ and after evaporation of the solvent the orange residue was chromatographed on silica gel to yield 2.83g (8mmol) (88%) (7-10- η - β -ionylideneacetonitrile)Fe(CO)₃ (60) in orange crystals m.p. = 119°C.

¹³C-NMR (50.4 MHz, CDCl₃) : 209.1 (s, CO); 136.9, 134.0 (2s, C(5), C(6)); 95.6 (s, C(9)); 87.4 (d, C(8)); 64.9 (d, C(7)); 41.8 (t, C(2)); 35.0 (t, C(4)); 34.6 (s, C(1)); 29.3 (q, C(13)); 28.7 (q, C(12)); 25.4 (d, C(10)); 22.9 (q, C(15)); 20.8 (q, C(14)); 18.5 (t, C(3)).

¹H-NMR (200 MHz, CDCl₃) : 5.87 (d, J=11.2, H-C(8)); 2.50 (s, 3H, H-C(15)); 2.04 (d, J=11.4, H-C(7)); 2.02 (m, H-C(4)); 1.82 (s, 3H, H-(14)); 1.45 (m, 4H, H-C(2), H-C(3)); 1.24, 1.13 (2s, 6H, H-C(12), H-C(13)); 0.49 (s, H-C(10)).

MS : 355 (M⁺); 327 (M⁺-CO); 299 (M⁺-2CO); 271 (M⁺-3CO); 355 (M⁺-Fe(CO)₃).

Microanalysis : calc. C : 60.89% H : 5.90%
 found C : 61.62% H : 6.27%

7.7 (2-5- η -5-(2',6',6'-Trimethyl-1'-cyclohexenyl)-3-methyl-2,4-pentadien-1-yl)Fe(CO)₃ (**61**)
 [(7-10- η - β -ionylideneacetaldehyde)Fe(CO)₃]

A solution of 590mg (1.66mmol) (7-10- η - β -ionylideneacetonitrile)Fe(CO)₃ (**60**) in 20ml dry ether under nitrogen was cooled to -78°C and 3.5ml (3.5mmol) DIBAH (1M in hexane) were added dropwise at this temperature. The solution was stirred for one hour, allowed to warm to RT and the excess reducing agent destroyed by the addition of 1.5ml of methanol. The reaction mixture was transferred under nitrogen to a 250ml flask and 50ml saturated NH₄Cl were added. This solution was stirred for 20 minutes and then acidified with 20ml 10% H₂SO₄. Extraction with 3 x 50ml ether, drying with Na₂SO₄, and filtration over a short aluminum oxide column gave 510mg (1.42mmol) (86%) (7-10- η - β -ionylideneacetaldehyde)Fe(CO)₃ (**61**).

¹³C-NMR (25.2 MHz, CDCl₃) : 209.9 (s, CO); 194.8 (d, C(11)); 136.8, 134.5 (2s, C(5), C(6)); 97.9 (s, C(9)); 88.6 (d, C(8)); 65.5 (d, C(7)); 56.2 (d, C(10)); 42.0 (t, C(2)); 35.2 (t, C(4)); 34.8 (s, C(1)); 29.6 (q, C(13)); 28.8 (C(12)); 23.0 (q, C(15)); 19.8 (q, C(14)); 18.7 (t, C(3)).

¹H-NMR (200 MHz, CDCl₃) : 9.45 (d, J=6.6, H-C(11)); 5.77 (d, J=11.3, H-C(8)); 2.55 (s, 3H, H-C(15)); 2.41 (d, J=11.2, H-C(7)); 2.02 (m, H-C(4)); 1.82 (s, 3H, H-(14)); 1.45 (m, 4H, H-C(2), H-C(3)); 1.26, 1.15 (2s, 6H, H-C(12), H-C(13)); 1.16 (d, J=6.7, H-C(10)).

MS : 274 (M⁺-3CO); 218 (M⁺-Fe(CO)₃).

7.8 (5-8- η -8-(2',6',6'-Trimethyl-1'-cyclohexenyl)-6-methyl-5,7-octadien-4-ol-2-one)Fe(CO)₃ (62**)**

Addition of 0.7ml (9.5mmol) acetone to a solution of 0.4g (1.1mmol) (7-10- η - β -ionylideneacetaldehyd)Fe(CO)₃ (**61**) in a methanolic KOH solution gave a dark red solution. Neutralisation after 3h at room temperature with acetic acid and evaporation of the solvents after extraction with ether gave a brown residue. Chromatography on silica gel (ether) gave the aldol product. No condensation products could be isolated. Yield 170mg (0.41mmol) (33%) of (5-8- η -8-(2',6',6'-trimethyl-1'-cyclohexenyl)-6-methyl-5,7-octadien-4-ol-2-one)Fe(CO)₃ (**62**).

¹³C-NMR (50.4 MHz, CDCl₃) : 212.5 (s, CO); 208.5 (s, C(13)); 135.4, 134.6 (2s, C(5), C(6)); 94.9 (s, C(9)); 84.9 (d, C(8)); 68.0 (d, C(11)); 64.3 (d, C(10)); 62.1 (d, C(7)); 50.8 (t, C(12)); 42.0 (t, C(2)); 35.1 (t, C(4)); 34.8 (s, C(1)); 30.8 (q, C(14)); 29.7 (q, C(17)); 28.8 (q, C(16)); 22.9 (q, C(18)); 19.9 (q, C(17)); 18.8 (t, C(3)).

¹H-NMR (400 MHz, CDCl₃) : 5.62 (d, J=10.8, H-C(8)); 4.16 (m, H-C(11)); 3.14 (d, J=3.1, -OH); 2.73 (d, 2H, J=6.0, H-C(12)); 2.22 (s, 3H, H-C(18)); 2.20 (s, 3H, H-C(14)) 2.02 (m, H-C(4)); 1.77 (s, 3H, H-C(17)); 1.67 (d, J=10.6, H-C(7)); 1.59-1.33 (2m, 4H, H-C(2), H-C(3)); 1.22, 1.16 (2s, 6H, H-C(12), H-C(13)); 0.83 (d, J=8.6, H-C(10)).

MS : 314 (M⁺-3CO-H₂O).

7.9 (4-7- η -7-(2',6',6'-Trimethyl-1'-cyclohexenyl)-5-methyl-2,4,6-heptatriene-1-nitrile)Fe(CO)₃ (65**)**

Under a nitrogen atmosphere 0.2ml (4mmol) acetonitrile were added to 20ml dry THF and cooled to -78°C. Slow addition of 2.2ml (4.5mmol) n-BuLi (1.6M in hexane) generated the lithium salt which precipitates. Subsequently, 0.8g (2.25mmol) (7-10- η - β -ionylideneacetaldehyde)Fe(CO)₃ (**61**) in 10ml of THF were added and a dark red solution was formed. The mixture was stirred at -78°C for 4h and then allowed to warm to RT overnight. Neutralisation with 10% HCl was followed by extraction with CH₂Cl₂. The organic phases were dried with Na₂SO₄ and after evaporation of the solvent the orange residue was chromatographed on silica gel to yield 0.65g (1.71mmol) (76%) (4-7- η -7-(2',6',6'-trimethyl-1'-cyclohexenyl)-5-methyl-2,4,6-heptatriene-1-nitrile)Fe(CO)₃ (**65**) as a yellow oil.

¹³C-NMR (50.4 MHz, CDCl₃) : 211.2 (s, CO); 152.4 (d, C(11)); 136.1, 134.7 (2s, C(5), C(6)); 96.5 (s, C(9)); 95.4 (d, C(12)); 86.4 (d, C(8)); 63.4 (d, C(7)); 59.6 (d, C(10)); 42.0 (t, C(2)); 35.1 (t, C(4)); 34.8 (s, C(1)); 29.7 (q, C(15)); 28.9 (q, C(14)); 23.0 (q, C(17)); 19.9 (q, C(16)); 18.7 (t, C(3)).

¹H-NMR (200 MHz, CDCl₃) : 6.78 (dd, J=15.6, 10.7, H-C(11)); 5.74 (d, J=11.1, H-C(8)); 5.43 (d, J=15.6, H-C(12)); 2.39 (s, 3H, H-C(17)); 2.17 (d, J=11.1, H-C(7)); 2.02 (m, 2H, H-C(4)); 1.82 (s, 3H, H-(16)); 1.62-1.40 (m, broad, 4H, H-C(2), H-C(3)); 1.26, 1.15 (2s, 6H, H-C(15), H-C(14)); 1.03 (d, J=10.7, H-C(10)).

7.10 (6-9- η -9-(2',6',6'-Trimethyl-1'-cyclohexenyl)-7-methyl-6,8-nonadien-5-ol)Fe(CO)₃ (66**)**

Addition of 1ml (1.6mmol) n-BuLi (1.6M in hexane) to a solution of 350mg (1mmol) (7-10- η - β -ionylideneacetaldehyde)Fe(CO)₃ (**61**) in dry THF forms a dark red solution. Neutralisation with 10% HCl and work-up with CH₂Cl₂ gave after drying, and chromatography on silica gel (ether/hexane 3/1) 360mg (0.86mmol) (86%) (6-9- η -9-(2',6',6'-trimethyl-1'-cyclohexenyl)-7-methyl-6,8-nonadien-5-ol)Fe(CO)₃ (**66**) as a yellow oil.

¹³C-NMR (25.2 MHz, CDCl₃) : 212.6 (s, CO); 135.0, 134.8 (2s, C(5), C(6)); 95.5 (s, C(9)); 84.8 (d, C(8)); 72.0 (d, C(11)); 68.4 (d, C(10)); 62.7 (d, C(7)); 42.3 (t, C(2)); 38.3 (t, C(12)); 35.4 (t, C(4)); 34.9 (s, C(1)); 29.7 (q, C(17)); 28.9 (C(16)); 28.0 (t, C(13)); 23.0 (t, C(14)); 22.7 (q, C(19)); 20.2 (q, C(18)); 18.7 (t, C(3)); 14.0 (q, C(15)).

¹H-NMR (200 MHz, CDCl₃) : 5.65 (d, J=10.7, H-C(8)); 3.75 (m, broad, H-C(11)); 2.23 (s, 3H, H-C(19)); 1.99 (m, 2H, H-C(4)); 1.79 (s, 3H, H-C(18)); 1.73 (d, J=10.7, H-C(7)); 1.70-1.30 (m, 10H, H-C(2), H-C(3), H-C(12), H-C(13), H-C(14)); 1.24, 1.15 (2s, 6H, H-C(12), H-C(13)); 1.02 (d, J=8.6, H-C(10)); 0.92 (t, 3H, H-C(15)).

MS : 258 (M⁺-Fe(CO)₃-H₂O); 243 (M⁺-Fe(CO)₃-H₂O-CH₃); 201 (M⁺-Fe(CO)₃-H₂O-C₄H₉).

7.11 (4-7- η -7-(2',6',6'-Trimethyl-1'-cyclohexenyl)-5-methyl-4,6-heptadien-3-ol-1-nitrile)Fe(CO)₃ (67)

Addition of 0.5ml (0.8mmol) n-BuLi (1.6M in hexane) to a solution of 0.1ml (2mmol) of acetonitrile and 180mg HMPTA in 20ml dry THF at -78°C followed by slow addition of 350mg (1mmol) (7-10- η - β -ionylideneacetaldehyde)Fe(CO)₃ (61) in 10ml THF formed a dark red solution. Neutralisation with H₂O and work-up with CH₂Cl₂ gave after drying, and chromatography on silica gel (ether/hexane 3/1) 170mg (0.42mmol) (42%) (4-7- η -7-(2',6',6'-trimethyl-1'-cyclohexenyl)-5-methyl-4,6-heptadien-3-ol-1-nitrile)Fe(CO)₃ (67) as a yellow oil.

¹³C-NMR (50.4 MHz, CDCl₃) : 211.9 (s, CO); 136.8, 134.5 (2s, C(5), C(6)); 117.5 (s, C(13)); 97.0 (s, C(9)); 86.6 (d, C(8)); 67.04 (d, C(11)); 64.1 (d, C(7)); 59.1 (d, C(10)); 42.1 (t, C(2)); 35.1 (t, C(4)); 34.8 (s, C(1)); 29.6 (q, C(15)); 28.8 (C(14)); 27.6 (t, C(12)); 22.9 (q, C(17)); 19.5 (q, C(16)); 18.7 (t, C(3)).

7.12 ((9E)-11-14- η -Vitamin A)Fe(CO)₃ (81)

620mg (1.2mmol) β -ionyltriphenylphosphonium bromide (79) were suspended in 15ml of dry THF and cooled to -70°C. Addition of 150mg (1.3mmol) (CH₃)₃COK in small portions generated the ylide and gave a dark red solution which was allowed to warm to -50°C. At this temperature 170mg (0.54mmol) (ethyl-2-5- η -6-oxo-3-methyl-2,4-hexadienoate)Fe(CO)₃ (80) dissolved in 2ml THF was slowly added and the reaction mixture warmed to 5°C. Half the solvent was evaporated, 5ml of H₂O added and the mixture extracted with methylene chloride. Filtration over aluminum oxide and subsequent chromatography on silica gel (hexane/ether 4/1) gave

a C₂₀-ester. 150mg (0.32mmol) of this ester was then dissolved in 10ml dry THF and cooled to -78°C. 0.6ml (0.6mmol) DIBAH (1M in hexane) were added dropwise and on completion of the reaction (TLC) hydrolysed first with methanol to destroy excess DIBAH, then with saturated NH₄Cl solution and 10% H₂SO₄. Extraction with methylene chloride and chromatography on Lichroprep (ether/hexane 1/1) gave ((9E)-11-14-η-vitamin A)Fe(CO)₃ (**81**) in a total yield of 130mg (0.305mmol) (66%).

¹³C-NMR (50.4 MHz, CDCl₃) : 211.5 (s, CO); 137.8 (s, C(9)); 137.0 (d, C(8)); 136.2 (s, C(6)); 131.7 (d, C(10)); 129.3 (s, C(5)); 126.3 (d, C(7)); 98.5 (s, C(13)); 85.0 (d, C(12)); 62.0 (t, C(15)); 60.3, 57.7 (2d, C(11), C(14)); 39.7 (t, C(2)); 34.1 (s, C(1)); 33.1 (t, C(4)); 28.8 (2q, C(16), C(17)); 21.6 (q, C(20)); 19.0 (t, C(3)); 18.2 (q, C(18)); 12.6 (q, C(19)).

¹H-NMR (400 MHz, CDCl₃) : 6.13 (d, J=16.1, H-C(8)); 5.96 (d, J=16.1, H-C(7)); 5.45 (d, J=10.5, H-C(12)); 5.21 (d, J=8.8, H-C(10)); 3.48 (m, broad, 2H, H-C(15)); 2.21 (s, 3H, H-C(20)); 2.14 (dd, J=10.5, 8.8, H-C(11)); 1.99 (m, 2H, H-C(4)); 1.85 (s, 3H, H-(19)); 1.68 (s, 3H, H-C(18)); 1.60-1.26 (2m, 4H, H-C(2), H-C(3)); 1.21 (t, J=6.8, H-C(14)); 1.01 (s, 6H, H-C(16), H-C(17)).

MS : 426 (M⁺); 342 (M⁺-3CO); 324 (M⁺-3CO-H₂O); 268 (M⁺-Fe(CO)₃-H₂O).

7.13 Synthesis and reactions of complexed Wittig-Horner synthons

7.14 (Ethyl-2-5- η -6-oxo-3-methyl-2,4-hexadienoate)Fe(CO)₃ (**80**)

Complexation using Fe₂(CO)₉ , Method b, Yield 80% of **80** as an oil.

¹³C-NMR (25.2 MHz, CDCl₃) : 195.9 (d, C(6)); 170.7 (s, C(1)); 85.3 (s, C(3)); 78.3 (d, C(4)); 60.5 (t, OCH₂CH₃); 52.7 (d, C(5)); 49.6 (d, C(2)); 18.6 (q, C(7)); 14.2 (q, OCH₂CH₃).

¹H-NMR (400 MHz, CDCl₃) : 9.39 (d, J=3.3, H-C(6)); 5.74 (d, J=7.9, H-C(4)); 4.12 (m, 2H, OCH₂CH₃); 2.53 (s, 3H, H-C(7)); 1.42 (dd, J=7.9, 3.2, H-C(5)); 1.24 (t, 3H, OCH₂CH₃); 1.19 (s, H-C(2)).

MS : 308 (M⁺); 280 (M⁺-CO); 252 (M⁺-2CO); 224 (M⁺-3CO).

7.15 (Ethyl-2-5- η -6-oxo-4-methyl-2,4-hexadienoate)Fe(CO)₃ (**82**)

Complexation using Fe₂(CO)₉ , Method b, Yield 84% of **82** as an oil.

¹³C-NMR (25.2 MHz, CDCl₃) : 195.0 (d, C(6)); 171.5 (s, C(1)); 103.0 (s, C(4)); 88.3 (d, C(3)); 60.9 (t, OCH₂CH₃); 57.6 (d, C(5)); 45.8 (d, C(2)); 19.0 (q, C(7)); 14.2 (q, OCH₂CH₃).

¹H-NMR (400 MHz, CDCl₃) : 9.55 (d, J=3.3, H-C(6)); 5.83 (d, J=8.0, H-C(3)); 4.16 (m, 2H, OCH₂CH₃); 2.54 (s, 3H, H-C(7)); 1.42 (d, J=8.0, H-C(2)); 1.32 (d, J=5.3, H-C(5)); 1.27 (t, 3H,

OCH_2CH_3).

MS : 308 (M^+); 280 ($\text{M}^+ - \text{CO}$); 252 ($\text{M}^+ - 2\text{CO}$); 224 ($\text{M}^+ - 3\text{CO}$).

7.16 (Ethyl-2-5- η -6-(diethylphosphonato)-4-methyl-2,4-hexadienoate) $\text{Fe}(\text{CO})_3$ (84)

Photolysis using $\text{Fe}(\text{CO})_5$, Method a, Yield 70% of 84 as an oil.

^{13}C -NMR (50.4 MHz, CDCl_3) : 209.3 (s, CO); 172.3 (s, C(1)); 101.8 (sd, $\text{J}(\text{P}, \text{C})=9.8$, C(4)); 84.5 (d, C(3)); 61.8 (td, $\text{J}(\text{P}, \text{C})=14.4$, $\text{PO}(\text{OCH}_2\text{CH}_3)_2$); 60.4 (t, OCH_2CH_3); 53.0 (dd, $\text{J}(\text{P}, \text{C})=6.9$, C(5)); 43.9 (d, C(2)); 28.5 (td, $\text{J}(\text{P}, \text{C})=140.3$, C(6)); 18.4 (q, C(7)); 16.3 (qd, $\text{J}(\text{P}, \text{C})=5.8$, $\text{PO}(\text{OCH}_2\text{CH}_3)_2$); 14.1 (q, OCH_2CH_3).

^1H -NMR (200 MHz, CDCl_3) : 5.74 (d, $\text{J}=7.9$, H-C(3)); 4.20-4.0 (m, 8H, H-C(6), OCH_2CH_3 , $\text{PO}(\text{OCH}_2\text{CH}_3)_2$); 2.24 (t, $\text{J}=5.6$, H-C(5)); 2.22 (s, 3H, H-C(7)); 1.35 (td, $\text{J}(\text{P}, \text{H})=1.5$, $\text{J}(\text{H}, \text{H})=7.0$, $\text{PO}(\text{OCH}_2\text{CH}_3)_2$); 1.25 (t, 3H $\text{J}=7.1$, OCH_2CH_3); 0.97 (d, $\text{J}=7.9$, H-C(2)).

7.17 (Diethyl-2-5- η -4,9-dimethyl-2,4,6,8,10-dodecapentaenedioate) $\text{Fe}(\text{CO})_3$ (83)

A solution of 580mg (2mmol) ethyl-6-(diethylphosphonato)-4-methyl-hexa-2,4-dienoate 73 in 25ml dry THF was cooled to -78°C and 1.2ml (1.92mmol) n-BuLi (1.6M in hexane) was slowly added. The dark red solution containing the ylide was warmed to -50°C and then re-cooled to -78°C . At this temperature 540mg (1.77mmol) (ethyl-2-5- η -6-oxo-4-methyl-2,4-hexadienoate) $\text{Fe}(\text{CO})_3$ (82) in 15ml THF was slowly added, the solution kept at -70°C

for 5h and then allowed to warm overnight to 5°C. Neutralisation with 10% HCl and extraction with CH_2Cl_2 gave after flash-chromatography on silica gel (ether/hexane 2/1) 0.66g (1.48mmol) (84%) (diethyl-2-5- η -4,9-dimethyl-2,4,6,8,10-dodecapentaene-dioate) $\text{Fe}(\text{CO})_3$ (**83**).

^{13}C -NMR (50.4 MHz, CDCl_3) : 209.1 (s, CO); 172.5 (s, C(1)); 166.9 (s, C(12)); 148.5 (d, C(10)); 137.2 (d, C(6)); 136.2 (d, C(8)); 133.6 (s, C(9)); 128.2 (d, C(7)); 117.1 (d, C(11)); 99.6 (s, C(4)); 84.6 (d, C(3)); 65.1 (d, C(5)); 60.6, 60.3 (2t, $\text{COOCH}_2\text{CH}_3$); 43.9 (d, C(2)); 19.2 (q, C(13)); 14.4, 14.3 (2q, $\text{COOCH}_2\text{CH}_3$); 12.7 (q, C(14)).

^1H -NMR (200 MHz, CDCl_3) : 7.35 (d, $J=15.6$, H-C(10)); 6.71 (dd, 14.5, 11.6, H-C(7)); 6.37 (d, $J=11.6$, H-C(8)); 6.15 (dd, $J=14.5$, 10.8, H-C(6)); 5.93 (d, $J=15.6$, H-C(11)); 5.73 (d, $J=8.4$, H-C(3)); 4.23 (q, $J=7.2$, C(12) OCH_2CH_3); 4.14 (m, C(12) OCH_2CH_3); 2.32 (s, 3H, H-C(13)); 2.15 (d, $J=10.8$, H-C(5)); 1.89 (s, 3H, H-C(14)); 1.36-1.24 (2t, 1d, 7H, 2 $\text{COOCH}_2\text{CH}_3$, H-C(2)).

MS : 444 (M^+); 416 ($\text{M}^+ - \text{CO}$); 388 ($\text{M}^+ - 2\text{CO}$); 360 ($\text{M}^+ - 3\text{CO}$).

**7.18 (Diethyl-2-5- η -2'-5'- η -4,4'-dimethyl-2,2',4,4',6,6'-
dodecapentaenedioate)bis-Fe(CO)₃ (**85**)**

A solution of 0.86g (2mmol) (ethyl-2-5- η -6-(diethylphosphonato)-4-methyl-hexa-2,4-dienoate)Fe(CO)₃ (**84**) in 25ml dry THF was cooled to -78°C and 1.25ml (1.92mmol) n-BuLi (1.6M in hexane) was slowly added. The dark red solution containing the ylide was warmed to -50°C and then re-cooled to -78°C. At this temperature 0.6g (1.9mmol) (ethyl-2-5- η -6-oxo-4-methyl-2,4-hexadienoate)-Fe(CO)₃ (**82**) in 15ml THF was slowly added and the solution was kept at -70°C for 5h and then allowed to warm overnight to 5°C. Neutralisation with 10% HCl and extraction with CH₂Cl₂ gave after flash-chromatography on silica gel (ether/hexane 2/1) 0.9g (1.61mmol) (85%) (diethyl-2-5- η -2'-5'- η -4,4'-dimethyl-2,2',4,4',6,6'-dodecapentaenedioate)bis-Fe(CO)₃ (**85**).

¹³C-NMR (50.4 MHz, CDCl₃) : 209.3 (s, CO); 172.4 (s, C(1)); 131.3 (d, C(6)); 99.1 (s, C(4)); 84.1 (d, C(3)); 65.2 (d, C(5)); 60.5 (t, OCH₂CH₃); 43.7 (d, C(2)); 19.0 (q, C(7)); 14.2 (q, OCH₂CH₃).

¹H-NMR (200 MHz, CDCl₃) : 6.08 (AA'XX', J=14.4, 10.6, -0.81, H-C(6)); 5.69 (d, J=7.8, H-C(3)); 4.13 (m, 2H, OCH₂CH₃); 2.31 (s, 3H, H-C(7)); 2.04 (AA'XX', J=14.4, 10.6, -0.81, H-C(5)); 1.26 (t, 3H, OCH₂CH₃); 1.19 (d, J=7.8, H-C(2)).

MS : 584 (M⁺); 556 (M⁺-CO); 528 (M⁺-2CO); 500 (M⁺-3CO) 472 (M⁺-4CO); 444 (M⁺-5CO); 416 (M⁺-6CO).

7.19 (2-5- η -2'-5'- η -4,4'-Dimethyl-2,2', 4,4',6,6'-dodecapentaen-1,1'-diol)bis-Fe(CO)₃ (86)

0.4g (0.7mmol) C₁₄-diester (85) were dissolved in 25ml THF, cooled to -78°C and 1.2ml (1.2mmol) DIBAH (1M in hexane) were added dropwise. The reaction was monitored on TLC and on completion 3ml methanol were added to remove excess DIBAH. Subsequently, the mixture was hydrolysed first with saturated NH₄Cl and then with 10% H₂SO₄. Extraction with methylene chloride and filtration over a short aluminum oxide column gave 315mg (0.63mmol) (90%) (2-5- η -2'-5'- η -4,4'-dimethyl-2,2',4,4',6,6'-dodecapentaen-1,1'-diol)bis-Fe(CO)₃ (86).

¹³C-NMR (50.4 MHz, d₆-acetone) : 212.7 (s, CO); 132.2 (d, C(6)); 97.8 (s, C(4)); 85.4 (d, C(3)); 66.3 (d, C(2)/C(5)); 64.5 (d, C(5)/C(2)); 60.5 (t, C(1)); 19.0 (q, C(7)).

¹H-NMR (200 MHz, CDCl₃) : 5.99 (AA'XX', J=14.4, 10.6, H-C(6)); 5.07 (d, J=8.2, H-C(3)); 3.76-3.62 (2m, 4H, H-C(1)); 2.23 (s, 3H, H-C(7)); 1.85 (AA'XX', J=14.4, 10.6, H-C(5)); 1.23 (td, J=8.2, 7.4, H-C(2)).

MS : 500 (M⁺); 472 (M⁺-CO); 444 (M⁺-2CO); 416 (M⁺-3CO); 388 (M⁺-4CO); 360 (M⁺-5CO); 332 (M⁺-6CO).

7.20 (2-5- η -2'-5'- η -4,4'-Dimethyl-2,2',4,4',6,6'-dodecapentaen-1,1'-dial)bis-Fe(CO)₃ (87)

0.1g (0.2mmol) C₁₄-diol (86) were dissolved in 5ml dry benzene and added to a slurry of Ag₂CO₃/Celite in benzene. This solution was refluxed for 3h during which time it turned black and the starting material disappeared. The mixture was then filtered

through Celite and concentrated under reduced pressure. Some decomposition products were removed by chromatography on silica gel (hexane/ether 1/1) which yielded 56mg (0.11mmol) (56%) (2-5- η -2'-5'- η -4,4'-dimethyl-2,2',4,4',6,6'-dodecapentaen-1,1'-dial)-bis-Fe(CO)₃ (**87**).

¹³C-NMR (50.4 MHz, d₆-acetone) : 196.5 (d, C(1)); 131.3 (d, C(6)); 100.4 (s, C(4)); 82.5 (d, C(3)); 65.7 (d, C(5)); 52.1 (d, C(2)); 19.1 (q, C(7)).

¹H-NMR (200 MHz, CDCl₃) : 9.32 (d, J=4.3, H-C(1)); 6.18 (AA'XX', J=14.6, 10.8, -0.71 H-C(6)); 5.67 (d, J=8.1, H-C(3)); 2.31 (s, 3H, H-C(7)); 2.30 (AA'XX', J=14.6, 10.8, -0.71, H-C(5)); 1.48 (dd, J=8.1, 4.3, H-C(2)).

MS : 496 (M⁺); 440 (M⁺-2CO); 412 (M⁺-3CO); 384 (M⁺-4CO); 356 (M⁺-5CO); 328 (M⁺-6CO).

7.21 (Ethyl-8-11- η -11-(2',6',6'-trimethyl-1'-cyclohexenyl)-4,9-dimethyl-2,4,6,8,10-undecapentaenoate)Fe(CO)₃ (88**)**

A solution of 290mg (1mmol) ethyl-6-(diethylphosphonato)-4-methyl-2,4-hexadienoate (**73**) in 25ml dry THF was cooled to -78°C and 1.2ml (1.92mmol) n-BuLi (1.6M in hexane) was slowly added. The dark red solution containing the ylide was warmed to -50°C and then re-cooled to -78°C. At this temperature 0.36g (1.0mmol) (7-10- η - β -ionylideneacetaldehyd)Fe(CO)₃ (**61**) in 15ml THF was slowly added and the solution was kept at -70°C for 5h and then allowed to warm overnight to 5°C. Neutralisation with 10% HCl and extraction with CH₂Cl₂ gave after flash-chromatography on silica gel (ether/hexane 2/1) 270mg (0.55mmol) (55%) (ethyl-8-

11- η -11-(2',6',6'-trimethyl-1'-cyclohexenyl)-4,9-dimethyl-2,4,6,8,10-undecapentaenoate)Fe(CO)₃ (**88**).

¹³C-NMR (25.2 MHz, CDCl₃) : 212.4 (s, CO); 167.3 (s, C(17)); 148.8 (d, C(15)); 138.6 (d, C(12)); 137.2 (d, C(13)); 135.1 (s, C(5)); 134.6 (s, C(6)); 132.5 (d, C(11)); 127.7 (s, C(14)); 116.4 (d, C(16)); 95.4 (s, C(9)); 85.2 (d, C(8)); 61.9 (d, C(7)); 61.5 (t, COOCH₂CH₃); 60.2 (d, C(10)); 42.2 (t, C(2)); 35.0 (t, C(4)); 34.8 (s, C(1)); 29.9 (q, C(19)); 29.7 (q, C(18)); 23.1 (q, C(21)); 20.2 (t, C(3)); 14.4, (q, COOCH₂CH₃); 12.7 (q, C(22)).

¹H-NMR (200 MHz, CDCl₃) : 7.24 (d, J=15.5, H-C(15)); 6.55 (dd, 14.5, 11.5, H-C(12)); 6.27 (d, J=11.5, H-C(13)); 6.05 (dd, J=14.5, 10.9, H-C(11)); 5.78 (d, J=15.5, H-C(16)); 5.58 (d, J=10.9, H-C(8)); 4.10 (q, 2H, J=7.2, COOCH₂CH₃); 2.25 (s, 3H, H-C(21)); 1.90 (d, 3H, J=10.9, H-C(7), H-C(4)); 1.85 (s, 3H, H-C(20)); 1.36-1.24 (m, 4H, H-C(2), H-C(3)); 1.26, 1.21, (2s, 6H, H-C(18), H-C(19)); 1.1 (s, 3H, COOCH₂CH₃); 0.95 (d, J=10.9 H-C(10)).

7.22 (Ethyl-2-5- η -6-acetoxy-4-methyl-2,4-hexadienoate)Fe(CO)₃ (**89**)

Complexation using Fe₂(CO)₉, Method b, Yield 65% of **89** as an oil.

¹³C-NMR (25.2 MHz, CDCl₃) : 172.1 (s, COCH₃); 170.3 (s, C(1)); 85.2 (s, C(4)); 79.1 (d, C(3)); 63.1 (t, C(6)); 60.5 (t, OCH₂CH₃); 56.8 (d, C(5)); 44.5 (d, C(2)); 20.7 (q, COCH₃); 18.1 (q, C(7)); 14.2 (q, OCH₂CH₃).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) : 5.72 (d, $J=7.9$, H-C(3)); 4.29 (dd, 2H, $J=7.0$, 1.8, H-C(6)); 4.11 (m, 2H, OCH_2CH_3); 2.26 (s, 3H, H-C(7)); 2.08 (s, 3H, COCH_3); 1.24 (t, 3H, OCH_2CH_3); 1.21 (t, $J=7.0$, hidden, H-C(5)); 1.01 (d, $J=7.9$, H-C(2));.

MS : 324 (M^+-CO); 296 (M^+-2CO); 268 (M^+-3CO).

7.23 (Diethyl-2-5- η -3-methyl-2,4-hexadienedioate) $\text{Fe}(\text{CO})_3$ (90)

Complexation using $\text{Fe}_2(\text{CO})_9$, Method b, Yield 86% of 90 as a orange oil which solidified below 0°C .

$^{13}\text{C-NMR}$ (50.4 MHz, CDCl_3) : 171.9, 170.9 (2s, C(1), C(6)); 103.7 (s, C(3)); 87.3 (d, C(4)); 60.4, 60.1 (2t, OCH_2CH_3); 48.7, 44.8 (2d, C(2), C(5)); 18.3 (q, C(7)); 13.9 (q, OCH_2CH_3).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) : 5.77 (d, $J=7.9$, H-C(4)); 4.22-4.05 (m, 4H, OCH_2CH_3); 2.54 (s, 3H, H-C(7)); 1.26 (m, 6H, OCH_2CH_3); 1.15 (d, $J=7.9$, H-C(5)); 0.99 (s, H-C(2)).

MS : 352 (M^+); 324 (M^+-CO); 296 (M^+-2CO); 268 (M^+-3CO).

7.24 (2-5- η -5-(2',6',6'-Trimethyl-1'-cyclohexenyl)-3-methyl-2,4-pentadien-1-ol) $\text{Fe}(\text{CO})_3$ (92)

[(7-10- η - β -ionylideneethanol) $\text{Fe}(\text{CO})_3$]

A solution of 6.33g (16.1mmol) (7-10- η - β -ionylideneacetic acid ethylester) $\text{Fe}(\text{CO})_3$ (91) in dry ether were cooled to -78°C and 40ml (40mmol) DIBAH (1M in hexane) was added dropwise. The reaction mixture was stirred overnight and then excess DIBAH was destroyed by the addition of 30ml of methanol. Subsequent

hydrolysis with 50ml saturated NH_4Cl and 20ml 10% H_2SO_4 gave an orange mixture which was extracted with 3 x 100ml CH_2Cl_2 . The organic solution was dried with Na_2SO_4 , the solvent was removed and the residue chromatographed on silica gel (ether/hexane 1/1). 4.37g (12.49mmol) (7-10- η - β -ionylideneethanol) $\text{Fe}(\text{CO})_3$ (92) (77%) was isolated as an oil.

^{13}C -NMR (25.2 MHz, CDCl_3) : 212.3 (s, CO); 136.8, 134.9 (2s, C(5), C(6)); 97.3 (s, C(9)); 85.5 (d, C(8)); 62.3 (d, C(10)/C(7)); 61.6 (t, C(11)); 59.0 (d, C(7)/C(10)); 42.1 (t, C(2)); 35.1 (t, C(4)); 34.8 (s, C(1)); 29.7 (q, C(13)); 28.8 (C(12)); 22.9 (q, C(15)); 18.9 (q, C(14)); 18.8 (t, C(3)).

^1H -NMR (200 MHz, CDCl_3) : 5.69 (d, $J=11.1$, H-C(8)); 3.8 (m, broad, H-C(11)); 2.3 (s, 3H, H-C(15)); 1.97 (m, broad H-C(4)); 1.84 (s, 3H, H-(14)); 1.82 (d, $J=11.1$, H-C(7)); 1.57-1.54 (m, 4H, H-C(2), H-C(3)); 1.24, 1.13 (2s, 6H, H-C(12), H-C(13)); 1.00 (d, $J=6.7$, H-C(10)).

MS : 304 (M^+-2CO); 276 (M^+-3CO); 220 ($\text{M}^+-\text{Fe}(\text{CO})_3$).

7.25 Decarbonylation Reactions with Concomitant Ligand Exchange

7.26 (Butadiene)Fe(CO)₂(P(Ph)₃) (97)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 1.33g (5.1mmol) triphenylphosphane were added. The suspension was stirred at 37°C and 0.5g (2.55mmol) (butadiene)Fe(CO)₃ (96) were added. On completion of the reaction (3.5h) the reaction was extracted with 7 x 11ml portions of hexane/ether 10/1 and the solvent was removed under reduced pressure. Chromatography on silica gel with hexane/ether 3/1 separates excess triphenylphosphane from the product. 0.81g (1.86mmol) (75%) (butadiene)Fe(CO)₂(P(Ph)₃) (97) were isolated as a yellow crystals m.p. 143-144°C.

TLC (hexane/ether 3/1) :

R_f (product) : 0.49, R_f P(Ph)₃ : 0.59,

R_f (butadiene)Fe(CO)₃ : 0.69

¹³C-NMR (25.2 MHz, CDCl₃) : 217.7 (sd, J(P,C)=13.5, CO); 136.0 (sd, J(P,C)=39.0, C(1')); 133.1 (dd, J(P,C)=10.8, C(2'), C(6')); 129.5 (dd, J(P,C)=2.1, C(4')); 128.0 (dd, J(P,C)=7.6, C(3'), C(5')); 84.4 (d, C(2), C(3)); 40.8 (t, C(1), C(4)).

¹H-NMR (200 MHz, C₆D₆) : 7.60 (m, H-C(2')); 7.14 (m, H-C(3'), H-C(4')); 4.93 (m, H-C(2), H-C(3)); 1.47 (m, H_B-C(1), H_B-C(4)); 0.00 (m, H_A-C(1), H_A-C(4)).

³¹P-NMR (80.7 MHz, C₆D₆) : 73.45 ppm

7.27 (Butadiene)Fe(CO)₂(P(OEt)₃) (98)

0.45g (4.0mmol) of trimethylamine oxide dihydrate was suspended in 10 ml of acetonitrile and 0.87g (5.25mmol) triethylphosphite were added. To this solution 0.5g (2.5mmol) of (butadiene)Fe(CO)₃ (96) were slowly added and the mixture stirred at 35-37° for 6.5h. During the reaction the colour of the mixture turns pale yellow. Addition of hexane produces a two-phase system which was extracted with 10 x 10ml portions of hexane. Solvent and excess triethylphosphite were removed under reduced pressure and the oily residue was filtered on a short aluminium oxide column using ether as the eluent and yielded 0.63g (1.89mmol) (76%) (butadiene)Fe(CO)₂(P(OEt)₃) (98).

TLC (hexane/ether 2/1) :

R_f (product) : 0.62

R_f (butadiene)Fe(CO)₃ : 0.69

¹³C-NMR (25.2 MHz, C₆D₆) : 216.3 (sd, J(P,C)=18.6, CO); 84.0 (d, C(2), C(3)); 60.4 (td, J(P,C)=3.7, P(OCH₂CH₃)); 39.5 (t, C(1), C(4)); 16.4 (qd, J(P,C)=6.4, P(OCH₂CH₃)).

¹H-NMR (200 MHz, C₆D₆) : 5.0 (m, H-C(2), H-C(3)); 3.80(dq, J=7.2, 7.2, P(OCH₂CH₃)₃); 1.64 (m, H_b-C(1), H_b-C(4)); 1.03 (t, J=7.0 P(OCH₂CH₃)₃); 0.03 (m, J(P,H)=6.0, H_a-C(1), H_a-C(4)).

IR (hexane) : 1993.0; 1934.5.

³¹P-NMR (80.7 MHz, C₆D₆) : 182.3ppm

⁵⁷Fe-NMR (12.97 MHz 1.1M, C₆D₆) : -26.0ppm, J(Fe,P)=86Hz.

7.28 (Butadiene)Fe(CO)₂(P(Et)₃) (99)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.6g (5.1mmol) triethylphosphane were added. To this suspension 0.5g (2.5mmol) (butadiene)Fe(CO)₃ (96) was added. The reaction mixture was stirred for 6h at 35-37°C and monitored by TLC. Subsequently the mixture was extracted with 7 x 11ml portions of hexane/ether 10/1, solvents and excess triethylphosphane were removed under reduced pressure and the yellow residue was filtered through a short aluminium oxide column with ether. Yield 0.66g (2.4mmol) (93%) (butadiene)-Fe(CO)₂(P(Et)₃) (99) as an oil.

¹³C-NMR (25.2 MHz, C₆D₆) : 217.4 (sd, J(P,C)=12.0, CO); 83.5 (d, C(2),C(3)); 38.3 (td, J(P,C)=3.0, C(1), C(4)); 21.0 (td, J(P,C)=24.0, P(CH₂CH₃)₃); 7.85 (qd, J(P,C)=1.8, P(CH₂CH₃)₃).

¹H-NMR (200 MHz, C₆D₆) : 4.89 (m, H-C(2), H-C(3)); 1.36 (m, H_b-C(1), H_b-C(4)); 1.20 (dq, J=7.5, 7.5, P(CH₂CH₃)₃); 0.74 (td J=7.5, 7.25, P(CH₂CH₃)₃); -0.36 (m, J(P,H)=6Hz, H_a-C(1), H_a-C(4)).

³¹P-NMR (80.7 MHz, C₆D₆) : 53.6 ppm

7.29 (Butadiene)Fe(CO)₂(CNC₆H₁₁) (100)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.57g (5.2mmol) cyclohexyl isocyanide were added. To this suspension 0.5g (2.5mmol) (butadiene)Fe(CO)₃ (96) was added. The reaction mixture was stirred overnight at 37°C and monitored by TLC. Subsequently the mixture was extracted with 7 x 11ml portions of hexane, solvents and excess

cyclohexyl isocyanide were removed under reduced pressure and the oily yellow residue was chromatographed on silica gel. Yield 470mg (1.70mmol) (68%) (butadiene) $\text{Fe}(\text{CO})_2(\text{CNC}_6\text{H}_{11})$ (**100**).

TLC (hexane/ether 8/1) : R_f (product) : 0.76.

^{13}C -NMR (25.2 MHz, C_6D_6) : 216.9 (s, CO); 84.6 (d, C(2), C(3)); 54.3 (d, CN-CH); 38.3 (t, C(1), C(4)); 32.9 (t, C(2')); 25.2 (t, C(4')); 22.9 (t, C(3')).

^1H -NMR (200 MHz, C_6D_6) : 5.07 (m, J=7.8, 5.0, 2.5 H-C(2), H-C(3)); 2.79 (m, broad, CN-CH); 1.54 (m, J=5, 2.5, 2.1, H_b -C(1), H_b -C(4)); 1.26 (m, CH_2); 1.08 (m, $2\times\text{CH}_2$); 0.92 (m, CH_2); 0.82 (m, CH_2); 0.1 (dd, J=7.8, 2.1, H_a -C(1), H_a -C(4)).

IR (CHCl_3) : 2140 (m, CN), 1990, 1930.

MS : 275 (M^+), 219 (M^+-2CO).

7.30 ((Z)-Pentadiene) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (**101**)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.87g (5.25mmol) triethylphosphite were added. To this suspension 0.5g (2.5mmol) ((Z)-pentadiene) $\text{Fe}(\text{CO})_3$ (**97**) was added. The reaction mixture was stirred for 6h at 37°C and monitored by TLC. Subsequently the mixture was extracted with 7 x 10ml portions of hexane, solvents and excess triethylphosphite were removed under reduced pressure and the yellow residue was filtered through a short aluminium oxide column with ether. Yield 0.83g (2.4mmol) (93%) ((Z)-pentadiene) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (**101**) as an oil.

TLC (hexane/ether 2/1) :

Rf (product) : 0.58

Rf (starting material) : 0.62

^{13}C -NMR (25.2 MHz, C_6D_6) : 216.5 (sd, $J(\text{P},\text{C})=19.0$, CO); 216.2 (sd, $J(\text{P},\text{C})=21.8$, CO); 88.5 (d, C(3)); 86.2 (d, C(2)); 59.9 (td, $J(\text{P},\text{C})=2.9\text{Hz}$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 49.9 (dd, $J(\text{P},\text{C})=3.6\text{Hz}$, C(4)); 39.2 (t, C(1)); 16.1 (qd, $J(\text{P},\text{C})=6.8\text{Hz}$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 13.4 (q, C(5)).

^1H -NMR (400 MHz, C_6D_6) : 5.12 (m, H-C(2)); 5.01 (m, H-C(3)); 3.82 (dq, $J=7.0$, 7.0, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 2.62 (dqdd, $J=8.0$, 7.0, 1.5, 1.5, H_b -C(4)); 1.82 (m, H_b -C(1)); 1.44 (ddd $J=9.0$, 2, 2, H_a -C(1)); 1.11 (d, $J=7.0$, CH_3); 1.08 (t, $J=7.0$ $\text{P}(\text{OCH}_2\text{CH}_3)_3$).

^{31}P -NMR (80.7 MHz, C_6D_6) : 178.7ppm

7.31 ((E)-4-Phenyl-3-buten-2-one) $\text{Fe}(\text{CO})_2(\text{P}(\text{Ph})_3)$ (102)

0.24g (2.2mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.77g (2.9mmol) triphenylphosphane were added. The suspension was stirred at RT and 0.5g (1.4mmol) ((E)-4-phenyl-3-buten-2-one) $\text{Fe}(\text{CO})_3$ 14 were added. On completion of the reaction (1h) the reaction was extracted with 7x11ml portions of hexane/ether 10/1 and the solvent was removed under reduced pressure. Chromatography on silica gel with hexane/ether 4/1 separated excess triphenylphosphane from the product. 0.49g (0.95mmol) (68%) ((E)-4-phenyl-3-buten-2-one) $\text{Fe}(\text{CO})_2(\text{P}(\text{Ph})_3)$ (102) were isolated as orange-red crystals, m.p. = 140-142°C.

TLC (hexane/ether 4/1) :

Rf (product) : 0.5 Rf ($\text{P}(\text{Ph})_3$) : 0.62

$^{13}\text{C-NMR}$ (25.2 MHz, C_6D_6) : 142.2 (s, C(2)); 135.5-125.4 (phenyl-C); 79.7 (d, C(4)); 63.1 (d, C(3)); 21.5 (q, C(1)).

$^1\text{H-NMR}$ (200 MHz, C_6D_6) : 7.41-7.07 (m, broad, phenyl); 6.66 (m, broad, phenyl); 5.77 (dd, $J(\text{P,H})=1.8$, $J(\text{H,H})=8.8$, H-C(3)); 2.47 (s, H-C(1)); 1.98 (dd, $J(\text{P,H})=0.4$, $J(\text{H,H})=8.8$, H-C(4)).

Microanalysis : calc : 69.27% C 4.80% H

found : 69.25% C 4.57% H

7.32 ((E)-4-Phenyl-3-buten-2-one)Fe(CO) $_2$ (P(OEt) $_3$) 103

0.45g (4.0mmol) of trimethylamine oxide dihydrate was suspended in 10 ml of acetonitrile and 0.87g (5.25mmol) triethylphosphite were added. To this solution 0.5g (1.4mmol) of ((E)-4-phenyl-3-buten-2-one)Fe(CO) $_3$ (14) were slowly added and the mixture stirred at 0° for 1h. During the reaction the colour of the mixture turns pale yellow. Addition of hexane produces a two-phase system which was extracted ten times with 10ml portions of hexane. Solvent and excess triethylphosphite were removed under reduced pressure and the oily residue was filtered on a short aluminium oxide column using ether as the eluent and yielded 0.45g (1.13mmol) (80.5%) ((E)-4-phenyl-3-buten-2-one)Fe(CO) $_2$ -P(OEt) $_3$ (103) as a dark red oil.

TLC (hexane/ether 2/1) :

R_f (product) : 0.36

R_f (starting material) : 0.54

$^{13}\text{C-NMR}$ (25.2 MHz, C_6D_6) : 215.3 (s, CO); 142.1 (s, C(2)); 138.3 (s, C(1')); 128.3 (d, phenyl); 127.1 (d, phenyl); 125.4 (d,

phenyl); 78.3 (d, C(3)); 61.0 (td, $P(OCH_2CH_3)_3$); 57.9 (d, C(4)); 22.2 (q, C(1)); 16.3 (qd, $P(OCH_2CH_3)_3$).

1H -NMR (400 MHz, C_6D_6) : 7.33 (m, H-C(3')); 7.11 (m, H-C(2')); 6.99 (t, H-C(4')); 5.49 (dd, $J(P,H)=2.4$, $J(H,H)=8.7$, H-C(3)); 3.89 (m $P(OCH_2CH_3)_3$); 2.9 (dd, $J(P,H)=7.3$ $J(H,H)=8.7$, H-C(4)); 2.28 (d, $J(P,H)=3.8$, H-C(1)); 1.04 (t, $P(OCH_2CH_3)_3$).

7.33 ((E)-4-Phenyl-3-buten-2-one)Fe(CO)₂(CNC₆H₁₁) (**104**)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.57g (5.2mmol) cyclohexyl isocyanide were added. To this suspension 0.72g (2.5mmol) (E-4-phenyl-3-buten-2-one)Fe(CO)₃ (**14**) was added. The reaction mixture was stirred at 0°C and monitored by TLC. Subsequently the mixture was extracted with 7x11ml portions of hexane, solvents and excess cyclohexyl isocyanide were removed under reduced pressure and the yellow residue was chromatographed on silica gel. Yield 610mg (1.7mmol) (68%) ((E)-4-phenyl-3-buten-2-one)Fe(CO)₂(CN-C₆H₁₁) (**104**) as orange crystals m.p. = 114°C.

TLC (hexane/ether 2/1) :

R_f (product) : 0.1

R_f (starting material) : 0.8

^{13}C -NMR (50.4 MHz, C_6D_6) : 214.0 (broad, CO), 147.6 (s, C(2)); 128.9 (s; C(1')); 128.5 (d, phenyl); 127.2 (d, phenyl); 124.0 (d, phenyl); 54.5 (d, CNCHR); 52.8 (d, C(3) or C(4)); 52.2 (d, C(3) or C(4)); 32.4 (t, cyclohexyl); 29.3 (q, C(1)); 24.9 (t, cyclohexyl); 22.9 (t, cyclohexyl).

$^1\text{H-NMR}$ (400 MHz, C_6D_6) : 7.40 (m, phenyl); 7.09 (m, phenyl); 6.93 (t, phenyl); 5.13 (d, $J=10.6$, H-C(3)); 4.15 (d, $J=10.6$, H-C(4)); 3.2-3.0 (m, broad, CNCH R); 2.46 (s, H-C(1)); 1.4-1.1 (m, cyclohexyl); 1.0-0.8 (m, cyclohexyl).

MS : 311 (M^+-2CO); 202 ($\text{M}^+-2\text{CO-CN}(\text{C}_6\text{H}_{11})$).

7.34 ((E)-4-Phenyl-3-buten-2-one)Fe(CO) $_2$ (CNCH $_2$ CO $_2$ Et) (105)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.28g (2.5mmol) ethyl isocyanoacetate were added. To this suspension 0.72g (2.5mmol) ((E)-4-phenyl-3-buten-2-one)Fe(CO) $_3$ (14) was added. The reaction mixture was stirred for 1h at RT and monitored by TLC. Subsequently the mixture is extracted with 7 x 11ml portions of hexane, solvents and excess isocyanoacetate were removed under reduced pressure and the yellow residue was chromatographed on silica gel. Yield 0.59g (1.6mmol) (64%) ((E)-4-phenyl-3-buten-2-one)Fe(CO) $_2$ -CNCH $_2$ CO $_2$ Et) (105) as orange-yellow crystals m.p. = 128°C.

$^{13}\text{C-NMR}$ (50.4 MHz, d_6 -acetone) : 129.1 (d, phenyl); 128.0 (s, C(1')); 127,3 (d, phenyl); 126.1 (d, phenyl); 77.4 (d, C(3)); 62.9 (t, OCH $_2$ CH $_3$); 46,4 (d, C(4)); 21.4 (q, C(1)); 14.25 (q, OCH $_2$ CH $_3$).

$^1\text{H-NMR}$ (400 MHz, C_6D_6) : 7.40-7.0 (m, phenyl); 5.84 (d, broad, H-C(3)); 4.50 (m, broad, H-C(4)); 4.30 (m, broad, OCH $_2$ CH $_3$); 2.50 (s, H-C(1)); 2.2 (s, CN-CH $_2$ COOEt); 1.32 (t, OCH $_2$ CH $_3$).

MS : 315 (M^+-2CO); 202 ($\text{M}^+-\text{CNCH}_2\text{COOEt}$).

Microanalysis : calc : 54.34% C 4.53% H

found : 55.03% C 4.53% H

7.35 (Hexadienal)Fe(CO)₂(P(Ph)₃) (106)

To a suspension of 0.45g (4mmol) trimethylamine oxide and 1.33g (5.1mmol) triphenylphosphane 0.6g (2.55mmol) (hexadienal)-Fe(CO)₃ (63) were added and the solution was stirred at 37° for 3h. The orange reaction mixture turned yellowish-brown. Extraction using hexane and subsequent chromatography on silica gel with hexane/ether 1/1 gave 0.69g (1.41mmol) (59%) (hexadienal)Fe(CO)₂(PPh₃) (106) as orange crystals, m.p. 130° C.

TLC (hexane/ether 1/1) :

R_f (product) : 0.44

R_f (starting material) : 0.42

¹³C-NMR (50.4 MHz, C₆D₆) : 214.9 (sd, J(P,C)=8.5, CO); 211.6 (sd, J(P,C)=4.7, CO); 196.3 (d, C(1)); 135.7 (sd, J(P,C)=40.7, C(1')); 132.9-127.0 (m, C(2'), C(3'), C(4')); 89.9 (d, C(4)); 82.7 (d, C(3)); 60.9 (dd, J(P,C)=1.7, C(5)/C(2)); 59.8 (dd, J(P,C)=4.2, (C(2)/C(5))); 17.9 (q, C(6)).

¹H-NMR (400 MHz, C₆D₆) : 9.1 (d, J=5.6, H-C(1); 7.6 (m, H-C(2')); 7.04 (m, H-C(3')); 6.94 (m, H-C(4')); 5.31 (m, (H-C(3))); 4.62 (dd, J=8.6, 3.8, H-C(4)); 1.06 (d, J=6.2, H-C(6)); 0.17 (m, H-C(2), H-C(5)).

IR (CHCl₃) : 1990 (s), 1932 (m), 1660 (s);

7.36 (Hexadienal)Fe(CO)₂(P(OEt)₃) (107)

0.9g (8.0mmol) trimethylamine oxide dihydrate were suspended in 20ml of acetonitrile and 1.32g (8.9mmol) triethylphosphite were added. After the addition of 1g (4.25mmol) (hexadienal)Fe(CO)₃ (63) the mixture was stirred for 4h at 37°C. The trimethylamine oxide dissolves during this time and the solution turns orange. The reaction was monitored with TLC and on completion was extracted with 8 x 11ml portions of hexane/ether 10/1. The solvents were evaporated, excess triethylphosphite was removed at 0.1 Torr and the yellow oil was filtered through a short aluminium oxide column. Chromatography on silica gel using hexane/ether 1/1 yielded 1.2g (3.26mmol) (76%) (hexadienal)-Fe(CO)₂(P(OEt)₃) (107).

TLC (hexane/ether 1/1) :

R_f (product) : 0.52

R_f (starting material) : 0.44

¹³C-NMR (25.2 MHz, C₆D₆) : 213.6 (sd, J(P,C)=16.5, CO); 211.5 (sd, J(P,C)=7.2, CO); 196.5 (d, C(1)); 89.1 (d, C(4)); 81.7 (dd, J(P,C)=3.0, C(3)); 61.1 (td, J(P,C)=5.3, P(OCH₂CH₃)₃); 58.4 (dd, J(P,C)=4.8, C(5)/C(2)); 56.9 (dd, J(P,C)=5.8, C(2)/C(5)); 18.8 (q, C(6)); 16.3 (qd, J(P,C)=6.1, P(OCH₂CH₃)₃).

¹H-NMR (200 MHz, C₆D₆) : 9.23 (d, J=6.2, H-C(1)); 5.20 (m, H-C(3)); 4.63 (dd, J=8.5, 5.0, H-C(4)); 3.83 (qd, J=7.5, 7.5, P(OCH₂CH₃)₃); 1.32 (d, J=6.0, H-C(6)); 1.12 (m, H-C(5)); 1.04 (t, J=7.0, P(OCH₂CH₃)₃); 0.91 (m, J=6.2, H-C(2)).

³¹P-NMR (80.7 MHz, C₆D₆) : 177.1ppm

7.37 (Hexadienal)Fe(CO)₂(P(Et)₃) (108)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.6g (5.1mmol) triethylphosphane were added. To this suspension 0.64g (2.5mmol) (hexadienal)Fe(CO)₃ (63) was added. The reaction mixture was stirred for 3.5h at 37°C and monitored by TLC. Subsequently the mixture was extracted with 7x11ml portions of hexane/ether 5/1, solvents and excess triethylphosphane were removed under reduced pressure and the dark red residue was chromatographed on silica gel with hexane/ether 2/1 . Yield 0.73g (2.25mmol) (90%) (hexadienal)-Fe(CO)₂(P(Et)₃) (108) as yellow crystals m.p. = 88-89°C.

¹³C-NMR (25.2 MHz, C₆D₆) : 215.4 (sd, J(P,C)=12.8, CO); 212.2 (sd, J(P,C)=5.4, CO); 196.8 (d, C(1)); 88.7 (d, C(4)); 81.8 (d, C(3)); 56.3 (dd, J(P,C)=5.4, C(5)/C(2)); 53.9 (dd, J(P,C)= 5.0, C(2)/C(5)); 20.2 (td, J(P,C)=25.2, P(CH₂CH₃)₃); 19.2 (q, C(6)); 7.75 (qd, J(P,C)=2.5, P(CH₂CH₃)₃).

¹H-NMR (400 MHz, C₆D₆) : 9.05 (d, J=7.2, H-C(1)); 5.06 (m, H-C(3)); 4.47 (dd, J=6.5, 1.5, H-C(4)); 1.47 (m, P(CH₂CH₃)₃); 1.17 (d, J=6.2, H-C(6)); 0.78 (m, P(CH₂CH₃)₃); 0.69 (m, H-C(5)); 0.63 (m, H-C(2)).

³¹P-NMR (80.7 MHz, C₆D₆) : 41.5ppm

7.38 (Hexadienal)Fe(CO)₂(CNC₆H₁₁) (109)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 0.57g (5.2mmol) cyclohexyl isocyanide were added. To this suspension 0.6g (2.5mmol) (hexadienal)Fe(CO)₃ (63) was added. The reaction mixture was stirred at 37°C for 3h and monitored by TLC. Subsequently the mixture was extracted with 7 x 11 ml portions of hexane, solvents and excess cyclohexyl isocyanide were removed under reduced pressure and the yellow residue was chromatographed on silica gel. Yield 540mg (1.7mmol) (69%) (hexadienal)Fe(CO)₂(CNC₆H₁₁) (109) as a yellow oil.

TLC (hexane/ether 1/1) :

Rf (product) : 0.13

Rf (starting material) : 0.42

¹³C-NMR (50.4 MHz, T = 343K, C₆D₆) : 215.4 (s, broad, CO); 214.6 (s, broad, CO); 195.1 (d, C(1)); 160.3 (s, broad, CN-R); 88.9 (d, C(4)); 80.4 (d, C(3)); 55.4 (d, C(5)/C(2)); 54.9 (d CN-CHR); 54.6 (d, C(2)/C(5)); 32.9 (t, cyclohexyl); 25.0 (t, cyclohexyl); 23.0 (t, cyclohexyl); 18.9 (q, C(6)).

¹H-NMR (400 MHz, C₆D₆) : 9.28 (d, H-C(1)); 5.43 (m, broad, H-C(3)); 4.69 (dd, J=8.6, 5.0, H-C(4)) 2.97 (m, broad, CNCHR); 1.22 (d, J=6.3, H-C(6)); 1.4-1.1 (m, cyclohexyl); 1.0-0.9 (m, cyclohexyl); 0.98 (m, H-C(5)); 0.86 (m, H-C(2)).

MS : 317 (M⁺); 289 (M⁺-CO); 261 (M⁺-2CO); 180 (M⁺-CO-CN(C₆H₁₁)).

7.39 (Hexadienal)Fe(CO)(P(OEt)₃)(P(Et)₃) (**110**)

0.5g (1.34mmol) (hexadienal)Fe(CO)₂(P(OEt)₃) (**107**) were irradiated for 12h at RT with a high pressure mercury lamp (Philips HPK, 125W) in 150ml of dry benzene in the presence of triethylphosphane. The reaction was monitored by TLC and on disappearance of the starting material the solvent and excess triethylphosphane was removed under reduced pressure. The red-brown oily residue was chromatographed on silica gel with ether/hexane 1/1. The major isomer crystallized in a yield of 150mg (0.3mmol) (22%) (hexadienal)Fe(CO)(P(OEt)₃)(P(Et)₃) (**110**), m.p. = 63-64°.

¹³C-NMR (50.4 MHz, C₆D₆) : 198.3 (d, (C(1))); 88.9 (d, C(4)); 75.6 (d, C(3)); 60.7 (td, J(P,C)=7.9, P(OCH₂CH₃)₃); 54.6 (dd, J(P,C)=10.7, 6.4 C(2)/C(5)); 53.0 (dd, J(P,C)=17.1, 5.4, C(5)/C(2)); 20.7 (td, J(P,C)=22.1, P(CH₂CH₃)₃); 19.1 (qd, J(P,C)=3.5, C(6)); 16.1 (qd, J(P,C)=6.2, P(OCH₂CH₃)₃); 7.8 (qd, J(P,C)=3.1, P(CH₂CH₃)₃).

¹H-NMR (400 MHz, C₆D₆) : 9.51 (d, J=7.3, H-C(1)); 5.11 (t broad, J=5.6, H-C(3)); 4.63 (qt broad, H-C(4)); 3.60 (qt, P(OCH₂CH₃)₃); 1.85 (m, P(CH₂CH₃)₃); 1.43 (dd, J(H,H)=6.2, J(P,H)=2.1, H-C(6)); 1.06 (qt P(OCH₂CH₃)₃); 0.97 (qt, P(CH₂CH₃)₃); 0.79 (m, H-C(5)); 0.37 (m, H-C(2)).

³¹P NMR (80.7 MHz, C₆D₆) : 173.2 (J(P,P)=38.0 ±0.3, P(OEt)₃);
41.2 (J(P,P)=38.0 ±0.3, P(Et)₃).

X-Ray Data

Summary of crystal data :

Asymmetric unit : $C_{19}H_{38}FeP_2O_5$

Molecular weight : 464.63

Unit cell data :

$a = 9.141(1) \text{ \AA}$, $b = 15.454(2) \text{ \AA}$, $c = 19.217 \text{ \AA}$, $\beta = 113.68(1)^\circ$

$V = 2714.7$, $Z = 4$ (racemate).

Space group $P2_1/c$.

The measurement was carried out on a Nicolet R3 diffractometer with λ (MoK) = $0.71069 \text{ \AA}$ with the ω -scan method. 4383 symmetry independent reflections were determined. The structure was solved using the SHELXTL 5.1 [190] program with a block cascade least-squares refinement.

7.40 ((Hexadienal)Fe(CO)₂(P(Ph₂)CH₂))₂ (111)

0.45g (4.0mmol) trimethylamine oxide dihydrate were suspended in 10ml of acetonitrile and 2.0g (5.2mmol) ethylenebis-(diphenylphosphino) were added. To this suspension 0.6g (2.5mmol) (hexadienal)Fe(CO)₃ (63) was added. The reaction mixture was stirred at 37°C and monitored by TLC. The white solid slowly dissolved in the reaction mixture and a yellow precipitate appeared. This was filtered off and dried. A second crop was isolated in the usual way by extraction with hexane/ether and chromatography. Yield 240mg (12%) (0.3mmol) ((hexadienal)Fe(CO)₂(P(Ph₂)CH₂))₂ (111), m.p. = 96-97°C.

¹³C-NMR (100 MHz, CDCl₃) : 213.9 (s, CO width 10 Hz); 211.1 (s, CO, width 4Hz); 197.8 (d, C(1)); 133.6 (sdd J(P,C)=39Hz, 4Hz, C(1')), 132.1 (dm C(2'), C(6')); 130.0 (d, C(4')); 128.6 (d, C(3'), C(5')); 90.2 (d, C(4)); 82.4 (d, C(3)); 60.3 (d, C(5)); 58.6 (d, C(2)); 27.1 (tt, J(P,C)=8Hz, (C₂H₂)₂); 18.0 (q, C(6)).

The same chemical shifts were determined for the two carbonyl signal at 25.2 MHz and at 100 MHz.

$^1\text{H-NMR}$ (200 MHz, C_6D_6) : 9.07 (d, $J=6.5$, H-C(1)); 7.58-7.23 (m, phenyl); 7.13-6.90 (m, phenyl); 5.15 (dd, $J=6.5$, 5.0, H-C(3)); 4.45 (dd, $J=8.0$, 5.0, H-C(4)); 2.54 ("s", $(\text{CH}_2)_2$); 0.85 (d, $J=6.0$, H-C(6)); 0.25 (m, H-C(2)); 0.05 (m, H-C(5)).

$^{31}\text{P-NMR}$: (80.7 MHz, C_6D_6) : 60.1ppm

7.41 (Hexadienol) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (112)

1g (2.7mmol) (hexadienal) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (107) were dissolved in 11ml of methanol/water 10/1 and cooled to 0°C. Subsequently, 0.15g NaBH_4 was added in small portions and the solution was stirred for 1h. After neutralisation with 10% HCl solution the reaction mixture was extracted with ether and methylene chloride. The solvents were removed and the highly viscous oil was chromatographed on aluminum oxide to yield 0.55g (1.5mmol) (55%) (hexadienol) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (112) as a yellow oil.

TLC (hexane/ether 1/1) :

R_f (product) : 0.23

R_f (starting material) : 0.52

$^{13}\text{C-NMR}$ (25.2 MHz, C_6D_6) : 215.0 (sd, $J(\text{P},\text{C})=10.4$, CO); 214.1 (sd, $J(\text{P},\text{C})=9.7$, CO); 86.1 (dd, $J(\text{P},\text{C})=0.5$, C(4)); 82.7 (dd, $J(\text{P},\text{C})=1.8$, C(3)); 65.7 (t, C(1)); 60.6 (td, $J(\text{P},\text{C})=5.0$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 60.2 (dd, $J(\text{P},\text{C})=5.0$, C(5)); 56.1 (dd, $J(\text{P},\text{C})=4.0$, C(2)); 19.2 (q, C(6)); 16.5 (qd, $J(\text{P},\text{C})=6.0$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$)).

$^1\text{H-NMR}$ (400 MHz, C_6D_6) : 4.73-4.63 (m, H-C(1)); 3.90-3.80 (m, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 3.90-3.80 (m, H-C(3)/H-C(4)); 3.68-3.64 (m, H-C(4)/H-C(3)); 1.36 (dd, $J=6.5$, 1.0, H-C(6)); 1.05 (t, $J=7.0$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 0.84 (m, H-C(2)); 0.76 (m, H-C(5)).

$^{31}\text{P-NMR}$ (80.7 MHz, C_6D_6) : 179.9ppm

7.42 [$(\text{Hexadienyl})\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)]\text{BF}_4$ (113)

0.55gr (1.3mmol) (hexadienol) $\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)$ (112) were dissolved at 0°C in 3ml acetic acid anhydrid and 0.25ml HBF_4 dissolved in 3ml acetic acid anhydride were slowly added. Subsequently, 20ml of ether was added to produce an oily precipitate. The supernatant solution was removed and the residue washed with ether and then dried. Yield of [$(\text{Hexadienyl})\text{Fe}(\text{CO})_2(\text{P}(\text{OEt})_3)]\text{BF}_4$ (113) : 0.5g (90%).

$^{13}\text{C-NMR}$ (25.2 MHz, d_6 -acetone) : 102.3 (d, C(3)); 101.8 (d, $J(\text{P,C})=3.0$, C(2)/C(4)); 91.8 (d, $J(\text{P,C})=1.0$, C(4)/C(2)); 88.9 (d, $J(\text{P,C})=7.0$, C(5)C(1)); 64.2 (td, $J(\text{P,C})=8.0$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$); 60.1 (d, $J(\text{P,C})=6.0$, C(1)/C(5)); 19.7 (q, C(6)); 15.0 (qd, $J(\text{P,C})=7.0$, $\text{P}(\text{OCH}_2\text{CH}_3)_3$).

7.43 (η^5 -Cyclopentadienyl) $\text{Co}(\text{CO})(\text{P}(\text{OEt})_3)$ (114)

0.9g (8.0mmol) trimethylamine oxide dihydrate were suspended in 20ml of acetonitrile and 1.32g (8.1mmol) triethylphosphite were added. After the addition of 0.88g (4.25mmol) (cyclopentadienyl) $\text{Co}(\text{CO})_2$ the mixture was stirred for 1h at RT. The trimethylamine oxide dissolves during this time and the solution turns dark brown. The reaction was monitored with TLC and on completion was extracted with 8 x 11ml portions of hexane/ether

10/1. The solvents were evaporated, excess triethylphosphite was removed at 0.1 Torr and the dark red oil was filtered through a short aluminium oxide column. Chromatography on silica gel using hexane/ether 1/1 yielded 0.66 g (2.1mmol) (51%) (η^5 -cyclopentadienyl)Co(CO)(P(OEt)₃) (**114**) as a dark red oil.

¹³C-NMR (25.2 MHz, C₆D₆) : 82.3 (d, J(P,C)=1.7, Cp); 60.6 (td, J(P,C)=1.6, P(OCH₂CH₃)₃); 16.5 (qd, J(P,C)=7.1, P(OCH₂CH₃)₃).

7.44 Addition of Lithium Dialkyl Phosphites to Cyclic Cationic Iron Complexes

General procedure for the addition of dialkyl phosphite anions to cyclohexadienyl and cycloheptadienyl iron complexes:

Under a nitrogen atmosphere 20ml of dry THF were cooled to -78°C in a dry ice/acetone bath. 1.8mmol dialkyl phosphite were dissolved and 1.8mmol n-butyllithium were added. The solution was warmed to -40°C and then cooled again to -78°C. After 10 minutes 0.5g (1.6mmol) [(cyclohexadienyl)Fe(CO)₃]⁺BF₄⁻ (**115**) were added in small portions and the mixture was slowly warmed. At around -50°C the murky reddish brown liquid turns red and becomes clear. The solvent was removed under reduced pressure and the oily residue was flash-chromatographed on a short silica gel column. A yellow oil was isolated in yields of 87% (dimethyl), 90% (diethyl) and 75% (diphenyl). Yields for (η^1, η^3 -2-(dimethylphosphonato)cycloheptenyl)Fe(CO)₃ (**121**) and (η^1, η^3 -2-(diethylphosphonato)cycloheptenyl)Fe(CO)₃ (**122**) were in a range between 85-90%.

Alternative work up:

Half the solvent was removed under reduced pressure and then 5ml of 10% H_2SO_4 solution was added at 0°C . The reaction mixture was extracted with 3x25ml portions of methylene chloride and the combined organic phases were dried with sodium sulphate. Removal of solvent yielded a yellow oil which was chromatographed on silica gel.

7.45 Spectroscopic data for :

7.46 (η^4 -5-(Dimethylphosphonato)-1,3-cyclohexadiene) $\text{Fe}(\text{CO})_3$
(118)

^{13}C -NMR (50.4 MHz, C_6D_6) : 211.0 (s, CO); 85.8, 85.0 (2dd, $\text{J}(\text{P},\text{C})=3.9$, C(2), C(3)); 60.2 (dd, $\text{J}(\text{P},\text{C})=10.1$, C(1)); 56.0 (dd, $\text{J}(\text{P},\text{C})=9.1$, C(4)); 53.0 (qd, $\text{J}(\text{P},\text{C})=6.5$, $\text{P}(\text{OCH}_3)_2$); 34.1 (dd, $\text{J}(\text{P},\text{C})=134.2$, C(5)); 25.5 (t, C(6)).

7.47 (η^4 -5-(Diethylphosphonato)-1,3-cyclohexadiene) $\text{Fe}(\text{CO})_3$ (119)

^{13}C -NMR (50.4 MHz, C_6D_6) : 211.8 (s, CO); 85.8 (d, C(2)); 85.5 (dd, $\text{J}(\text{P},\text{C})=4.1$, C(3)); 61.8 (td, $\text{J}(\text{P},\text{C})=6.6$, $\text{P}(\text{OCH}_2\text{CH}_3)_2$); 61.0 (dd, $\text{J}(\text{P},\text{C})=9.7$, C(1)); 57.7 (dd, $\text{J}(\text{P},\text{C})=8.9$, C(4)); 35.0 (dd, $\text{J}(\text{P},\text{C})=134.1$, C(5)); 26.1 (t, C(6)); 16.5 (qd, $\text{J}(\text{P},\text{C})=4.9$, $\text{P}(\text{OCH}_2\text{CH}_3)_2$).

7.48 (η^4 -5-(Diphenylphosphonato)-1,3-cyclohexadiene) $\text{Fe}(\text{CO})_3$
(120)

^{13}C -NMR (50.4 MHz, C_6D_6) : 210.7 (s, CO); 129.5, 128.8, 125.4, 120.8 ($\text{P}(\text{OPh})$); 85.9, 85.5 (2dd, $\text{J}(\text{P},\text{C})=3.3$, C(2), C(3)); 59.6

(dd, $J(P,C)=8.6$, $C(1)/C(4)$); 54.8 (dd, $J(P,C)=11.4$, $C(4)/C(1)$); 34.9 (dd, $J(P,C)=131.4$, $C(5)$); 25.5 (t, $C(6)$).

7.49 (η^1, η^3 -2-(Dimethylphosphonato)cycloheptenyl)Fe(CO)₃ (121)

¹³C-NMR (50.4 MHz, C₆D₆) : 214.2 (s, CO); 99.8 (dd, $J(P,C)=4.1$, $C(4)$); 80.8 (d, $C(5)$); 57.3 (d, $C(3)$); 53.0, 52.8 (2qd, $J(P,C)=7.6$, 7.4, $P(O\text{CH}_3)_2$); 45.3 (dd, $J(P,C)=124.0$, $C(2)$); 39.2 (td, $J(P,C)=7.2$, $C(7)$); 27.7 (t, $C(6)$); 17.9 (dd, $J(P,C)=11.6$, $C(1)$).

¹H-NMR (400 MHz, C₆D₆) : 4.65 (t, H-C(5)); 4.15 (t, $J(H,H)=7.0$, H-C(4)); 3.97 (t, $J(H,H)=6.8$, H-C(3)); 3.43, 3.38 (2d $J(P,C)=10.5$, 10.5, $P(O\text{CH}_3)_2$); 3.32 (dt, $J(P,C)=21.9$, $J(H,H)=6.7$, H-C(2)); 2.58 (m, 1H, H-C(6)); 2.12 (m, 1H, H-C(6)); 1.9-1.8 (m, 2H, H-C(7)); 1.30 (m, broad, H-C(1)).

7.50 (η^1, η^3 -2-(Diethylphosphonato)cycloheptenyl)Fe(CO)₃ (122)

¹³C-NMR (50.4 MHz, C₆D₆) : 213.8 (s, CO); 99.3 (dd, $J(P,C)=4.1$, $C(4)$); 80.2 (d, $C(5)$); 61.9, 61.5 (2td, $J(P,C)=7.5$, 7.3, $P(O\text{CH}_2\text{CH}_3)_2$); 57.3 (d, $C(3)$); 45.5 (dd, $J(P,C)=124.4$, $C(2)$); 39.0 (td, $J(P,C)=7.1$, $C(7)$); 27.3 (t, $C(6)$); 17.9 (dd, $J(P,C)=11.6$, $C(1)$); 16.1, 16.0 (2qd $J(P,C)=2.3$, 2.7, $P(O\text{CH}_2\text{CH}_3)_2$).

¹H-NMR (400 MHz, C₆D₆) : 4.45 (t, H-C(5)); 4.0-3.8 (m, 6H, H-C(3), H-C(4), $P(O\text{CH}_2\text{CH}_3)_2$); 3.34 (dt, $J(P,H)=21.3$, $J(H,H)=6.5$, H-C(2)); 2.76 (m, 1H, H-C(6)); 2.14 (m, 1H, H-C(6)); 2.0-1.9 (m, 2H, H-C(7)); 1.39 (m, broad, H-C(1)); 1.03 (2t, $P(O\text{CH}_2\text{CH}_3)_2$).

7.51 Spectroscopic Data of (Heterodiene)Fe(CO)₃ Complexes

For the synthesis of the following compounds see Chapter 7.3.

((E)-2-Butenal)Fe(CO)₃ (124)

¹³C-NMR (25.2 MHz, C₆D₆) : 208.5 (s, CO); 123.1 (d, C(1)); 88.7 (d, C(2)); 59.8 (d, C(3)); 17.2 (q, C(4)).

(2-Methyl-propenal)Fe(CO)₃ (125)

¹³C-NMR (25.2 MHz, C₆D₆) : 208.7 (s, CO); 123.8 (d, C(1)); 102.7 (s, C(2)); 45.7 (t, C(3)); 16.5 (q, CH₃-C(2)).

(2-Methyl-2-butenal)Fe(CO)₃ (126)

¹³C-NMR (25.2 MHz, C₆D₆) : 120.8 (d, C(1)); 103.3 (s, C(2)); 61.8 (d, C(3)); 14.2, 12.6 (2q, C(4), CH₃-C(2)).

(3-Methyl-3-buten-2-one)Fe(CO)₃ (130)

¹³C-NMR (25.2 MHz, C₆D₆) : 208.0 (s, CO); 143.3 (s, C(2)); 94.7 (s, C(3)); 45.0 (t, C(4)); 18.7, 17.8 (2q, C(1), CH₃-C(3)).

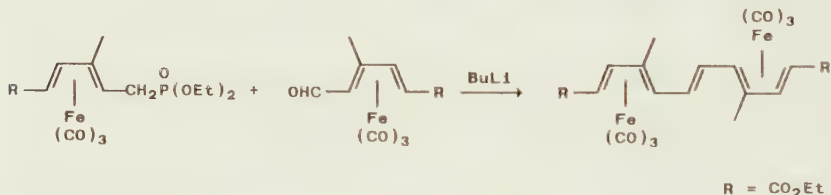
(4-penten-3-one)Fe(CO)₃ (131)

¹³C-NMR (25.2 MHz, C₆D₆) : 207.5 (s, CO); 150.9 (s, C(3)); 76.5 (d, C(4)); 38.6 (t, C(5)); 27.6 (t, C(2)); 11.2 (q, C(1)).

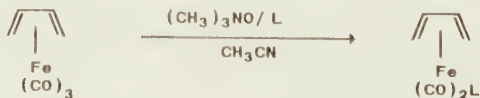
8. SUMMARY

The principal results of this thesis can be summarized as follows :

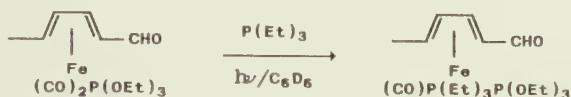
Aldol condensations, reductions, and Wittig reactions of (ionone)Fe(CO)₃ and (diene)Fe(CO)₃-type complexes gave synthetically interesting products, notably (vitamin A)Fe(CO)₃. Highly stereoselective formation of (E)-substituted double bonds has been achieved by the use of bifunctionalized (diene)Fe(CO)₃ complexes in Wittig-Horner reactions. Reduction of the dinuclear C₁₄-diester complex, followed by oxidation yielded the C₁₄-dialdehyde complex which can be regarded as a synthon for isoprenoid natural products.



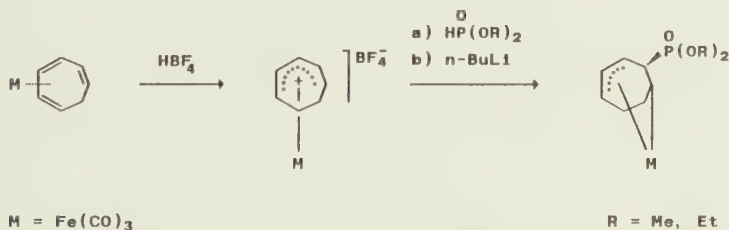
A novel method has been developed for selectively exchanging one carbonyl ligand of acyclic (diene)Fe(CO)₃ and (enone)Fe(CO)₃ complexes by a phosphane, phosphite or isonitrile ligand. This efficient ligand exchange reaction is effected by the use of trimethylamine oxide in a complexing solvent.



By irradiating (hexadienal)Fe(CO)₂(P(OEt)₃) in the presence of triethylphosphane the first iron diene complex with three different η^2 -ligands was synthesized. Thereby, a complex with planar chirality is transformed into a compound with additional central chirality at the iron atom.



The addition of lithium dialkyl phosphites to metal-coordinated cyclic carbenium ions is a fast and efficient method for the synthesis of complexed cyclic phosphonates. Depending on the cationic complex employed different products, notably the unusual one shown below, are formed.



In a ⁵⁷Fe-NMR study a series of methyl and phenyl substituted (enone)Fe(CO)₃ complexes were synthesized and their ⁵⁷Fe chemical shifts determined and analyzed. The low thermal stability of these complexes is reflected in their very high chemical shifts relative to (butadiene)Fe(CO)₃. Substitution by phenyl has been found to deshield more than substitution by methyl.

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